1957

Characteristics of the solid state transformations in uranium

Harold Holmes Klepfer
Iowa State College

NOTE TO USERS

CHARACTERISTICS OF THE SOLID STATE TRANSFORMATIONS IN URANIUM

by

Harold Holmes Klepfer

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Metallurgy

Approved:

Signature was redacted for privacy.
In Charge of Major Work

Signature was redacted for privacy.
Head of Major Department

Signature was redacted for privacy.
Dean of Graduate College

Iowa State College

1957

TABLE OF CONTENTS

INTRODUCTION

The thermal expansion of uranium and the nature of allotropic transformation processes in uranium are of obvious interest in predicting or understanding the effects of thermal cycling on components fabricated of uranium such as nuclear fuel elements. Quite apart from this possible immediate practical interest is the theoretical interest in the transformation processes themselves. The purpose of the present investigation is to determine the temperature dependence of the lattice parameters of uranium from room temperature to the melting point and to provide experimental data on the general characteristics and kinetics of the allotropic transformations in uranium. Toward this end high-temperature x-ray diffraction, electrical resistivity, and sonic experimental techniques were employed. The data presented are interpreted in terms of the known physical, mechanical, and structural properties of the metal and are intended as a contribution toward the complete experimental and theoretical description of the allotropic transformation processes in pure uranium.

Metallic uranium is known to exist in three allotropic forms between room temperature and its melting point. The crystal structures of all three phases are known. The room temperature alpha form is orthorhombic and is stable at temperatures up to 668°C, the beta form is tetragonal and is stable in the temperature range 668 to 774°C, and the gamma

form is body-centered cubic and is stable from 774°C to the melting point (1132°C). The transformation temperatures reported vary over a fairly wide temperature range presumably due to variations in the purity of the metal and to the cooling and heating rates employed.

The structure of the low temperature or alpha phase was first determined by Jacob and Warren (1). It is orthorhombic of space group Cmcm with four atoms per unit cell. Tucker (2) has discussed the structure from the standpoint of chemical bonding and presents evidence for covalent bonding between atoms in the corrugated (010) sheets. The covalent bonding is proposed as the basis for the commonly known metalloid-like characteristics of this phase. The lattice parameters of this phase as a function of temperature from -253°C to 640°C have been recently reported by Bridge, Schwartz, and Vaughan (3).

Beta uranium, the form stable between about 670°C and 770°C, has a complex tetragonal cell of 30 atoms and space group P4/mnm or P4/nm. The exact space group and precise atomic positions have been debated in a series of papers by Tucker and Senio and Thewlis and Steeple. The status of this debate was reviewed in a joint statement by these authors (4). The high hardness and low ductility of beta uranium is consistent with the complexity of its structure.

Wilson and Rundle (5) established the structure of the high temperature gamma phase as body centered cubic with two

atoms per unit cell. This structure is more typical of metals, and this fact is reflected in the mechanical properties of uranium above about 770°C.

An authoritative review of the physical and mechanical properties of the three allotropic forms of uranium is to be found in the Geneva Conference Report in the chapters by Foote (6) and Howe (7). Cahn's paper on the modes of deformation in alpha uranium (8) and Holden's on the deformation of beta uranium (9) are also of interest. In a recent paper by Friedel (10) proposals were made on a semi-empirical basis about the electronic band structure in the three phases. These proposals attempt to explain the temperature dependence of the specific heat, magnetic susceptibility, and electrical resistivity, as well as the temperature dependence of the alpha phase lattice parameters as reported by Saller (11).

The complete experimental description of an allotropic transformation process would include (a) a determination of the general features of the transformation in terms of the resulting macroscopic and microscopic changes in the material, (b) a qualitative and quantitative determination of the kinetics of the reaction, and (c) a determination of the crystallographic orientation relationship between parent and product phase. Theoretical, mechanistic models have been put forth which show promise of permitting the analytical deduction of such a description. However, in these models certain experimental parameters are required. In particular the lattice

parameters of the phases involved at the transformation temperatures are needed for the calculation of the crystallographic features. The elastic constants of the phases, grain boundary energy parameters, and mobility parameters for the movement of atoms and/or imperfections in the lattices are also necessary for the calculation of the kinetic features.

Before further discussion of transformation processes it is felt necessary to clarify the ambiguity in the terminology which has arisen in the literature in this field. Past practice has been generally to classify allotropic transformations either as classical nucleation and growth transformations or as martensitic or diffusionless transformations. The use of "martensitic" or "diffusionless" when applied as generic terms to solid state transformations, however, has been weakened by recent experimental developments.

The term "martensitic" has arisen historically in grouping together phase changes in metals and alloys having features similar to those for the austenite (face centered cubic) to martensite (body centered tetragonal) transformation in steel. This particular transformation has been studied in great detail in various iron alloys. Important features of this transformation include the following:

(1) The transformation is athermal. That is it proceeds only when the termperature is changing, but ceases when the temperature is held constant. Thus, between two critical temperatures, the temperature at

which the transformation starts (M_s) and some lower temperature at which the transformation is complete (M_f), the percent transformed is observed to be a function of the temperature only. Small discreet volumes within the parent phase transform in a very short period of time. The velocity of propagation of the new phase approaches the velocity of sound in the matrix material.

(2) The new phase appears as discreet lenticular regions of limited size within the parent phase. These lenticular or disk-shaped regions appear as "needles" upon microscopic examination. The formation of these martensite needles is believed to be accomplished by the cooperative movement of a large number of atoms through distances less than an atomic spacing. The martensite regions are left sheared with respect to the parent lattice by this process. This shear and the volume change involved produces characteristic surface relief effects. Furthermore, this process like other processes in solids involving the rapid movement of atoms in phase produces sonic activity which can be detected.

(3) There is a definite orientation relationship between the product phase and the parent phase.

(4) There is a certain degree of reversibility in the orientation. The effect is as if there were a

strain "memory" in the transformed metal which favors the retransformation to the original orientation. In particular a needle of martensite which has been formed on cooling retransforms on heating to austenite of the original orientation.

The term "diffusionless" when applied to this and other alloy transformations having similar characteristics was intended to stress that they were too rapid to allow any composition change in the phases. Any composition adjustment would require diffusion, a slow process in solids.

Classical nucleation and growth transformations in alloys do involve a composition change. Furthermore, from the temperature dependence of the rate of transformation an activation energy can be determined which is found to be comparable to that for the diffusion of one of the alloying elements in the parent matrix.

The implication of a composition criterion in distinguishing between diffusionless or martensitic and classical nucleation and growth reactions is obviously not very meaningful in the case of phase changes in pure metals.

Even in the case of alloys at least two cases apparently strain the connotations of the terms. The bainite reaction in iron-carbon alloys has some characteristics definitely similar to those of the martensite reaction, but the rate is not rapid and indeed is apparently controlled by the diffusion of carbon in the product phase (12). The tetragonal

to orthorhombic transformation of a uranium-0.3 wt. % chromium alloy at room temperature has been shown by Holden (13) to proceed isothermally by the slow growth of martensite-like needles without any change in composition.

The terminology accepted for the purpose of discussion of allotropic transformations in this thesis is that suggested by Knapp and Dehlinger (14). Transformations will be distinguished on the basis of the nature of the boundary between the two phases during nucleation and growth. Incoherent nuclei are those separated from the parent phase by a large-angle grain boundary in such a way that movement of the boundary entails the transfer of material across a region of highly disordered metal and takes place atomwise. Transformations involving incoherent nuclei are expected to have characteristics similar to those of classical nucleation and growth transformations. Coherent nuclei are those separated from the parent phase by a small-angle grain boundary in such a way that movement of the boundary involves the co-operative movement of a large number of atoms through less than interatomic distance. The typical martensitic reactions evidently involve such nuclei as do the bainite and low temperature uranium-chromium alloy transformations. The non-kinetic martensitic characteristics such as nuclei shape, definite orientation relationship, surface relief effects, and reversibility can be deduced from strain energy considerations for the formation of coherent nuclei. The rate of growth of

coherent nuclei is not restricted by this definition, and diffusion, availability of modes of stress relief, or crystal imperfection of the parent lattice are permitted among possible rate controlling factors. The nature of a transformation then is designated by specification of the type of nuclei and probable nature of the rate controlling factor for growth.

Phase transformations in solids have received considerable attention in recent years, particularly the so-called diffusionless or martensitic transformations. Authoritative reviews covering the very broad spectrum of this work are available (15, 16, 17). That theory believed pertinent to the present investigation will be discussed in the following paragraphs.

The problem of nucleation in solids has been examined notably by Turnbull (18), Cohen (19), and by others. Knapp and Dehlinger (14) have recently made certain proposals with respect to coherent nucleation. Since the surface energy and strain energy barrier to the growth of nuclei of a very small size is prohibitive, some mechanism of formation of nuclei of a certain critical size is required. Statistical fluctuations have been proposed as a solution to this dilemma. The alternate suggestion is the existence of an "embryonic" or "preformed nucleus". These "preformed nuclei" consist of regions in the parent phase of atomic arrangement approximating that of the product phase. Upon sufficient cooling below (or heating above) the equilibrium temperature for the trans-

formation, these regions become nuclei of the product phase of the critical size and begin to grow. Knapp and Dehlinger propose that such preformed nuclei arise from suitable combinations of the dislocations which are always present in the parent phase. This concept of these ready-made critical-size regions is apparently necessary to explain nucleation for transformations in solids at the small extent of supercooling (or superheating) experimentally observed. For the investigation at hand it is important to note two proposals made by Knapp and Dehlinger. The first is that at any given temperature below some critical temperature, corresponding to the M_s temperature in steel, only a certain fraction of these ready-made regions become activated for growth. As the temperature is decreased, more of these preformed nuclei begin to grow. The second is that external pressure on the metal effects the number of these regions activated.

Knapp and Dehlinger have also considered the kinetics of processes involving the growth of plate-like or disk-shaped coherent nuclei (14). They write the driving force for the formation of a nucleus as

$$f = f_c + e_v = f_c + e_\epsilon + e_s \qquad 1.$$

where f_c is the chemical free energy change involved which is calculated from thermodynamic data and is therefore independent of the size of the nucleus; e_v is the total distortion energy involved. The distortion energy is made up of two terms. The first is the strain energy e_ϵ arising from

the volume change and the requirement of coherence, and the second is the surface energy e_s at the boundary between the two phases. As the size of the nucleus increases by growth of the disk in diameter, at a given temperature below the temperature at which $f_c = 0$, the term e_ϵ is shown to be expected to decrease faster than e_s increases so that e_v becomes less positive as the process continues. The value of f_c is, of course, fixed by the temperature and must be negative for the transformation to take place at all under these conditions. Thus, the effective driving force increases as this growth goes on. When this process is halted by intersection with some obstacle such as a grain boundary, the disk-like nucleus tends to grow by increasing in thickness. This process is shown to increase the strain energy term e_ϵ faster than the surface energy term e_s decreases. Thus, the total distortion energy e_v becomes more positive until it is equal to the negative chemical term. When this happens the driving force or change in free energy of the system for further growth is zero and the process stops.

For a given value of the driving force the rate of movement of the boundary between the phases depends on the mechanism involved in this movement. If this movement involves, as has been suggested, a plane of dislocations moving into the parent phase, then the rate will be determined by the velocity at which the dislocations can move into the matrix under the influence of the given driving force. For the iron-

carbon martensitic reaction, Knapp and Dehlinger show that this velocity approaches the speed of sound in the metal. However, it is not unreasonable to believe that for coherent transformations in other metals and alloys where the maximum driving force may also be less, as it certainly must be in cases of transformation at only a few degrees from the equilibrium temperatures, the rate of movement of a dislocation boundary may be much slower. This might be especially expected when one or both of the structures involved are complex. On the basis of these arguments it is not unreasonable to expect that rather slow transformation is possible by a process involving coherent nuclei.

The literature was reviewed to establish the status of the experimental description of the allotropic transformations in uranium and to determine the availability of the parameters necessary for the theoretical calculations.

There has been apparently conflicting evidence as to whether the alpha-beta transformation in pure uranium is of the general martensitic or of the classical nucleation and growth type. Much of this conflict, however, seems to arise from the lack of precision in the terminology. Little direct evidence is available on the nature of the beta-gamma transformation.

Both transformations have been successfully employed in the phase change method of single crystal growth (9, 20). Both transformation temperatures can be greatly depressed by

rapid quenching (21). These are features which were taken as more commonly characteristic of classical nucleation and growth reactions. The time-temperature-transformation curves for uranium-chromium alloys were studied by White (22). He found a high temperature "C" curve which was established as that for a diffusion controlled process. A second low temperature "C" curve was also reported which was classified as that for a martensitic transformation, non-typical in its kinetic features. As the chromium content was lowered the temperature at which this latter type of transformation became predominant was found to increase. Holden (13) established that the transformation of these alloys at room temperature involved the isothermal growth of martensite-like needles and established an orientation relationship between the two phases. Butcher and Rowe (23) reported a nearly equivalent habit plane and orientation relationship for the low-temperature transformation of these low-chromium uranium-chromium alloys. Butcher (24) has explained the orientation of alpha grains of pure uranium resulting from the quench of a single beta crystal on the basis of this orientation relationship.

Other characteristics of this pure uranium transformation were discussed by Butcher (24) including the randomization of the orientation of grains after thermal cycling through the transformation. He also presented indirect evidence for the progressive hardening of the alpha lattice following thermal cycling. His conclusion was that the beta to alpha transforma-

tion in pure uranium must involve martensitic nucleation and growth. No data relating to the kinetic features and no direct determination of the orientation relationships involved in the allotropic transformations of pure uranium have been reported.

The elastic constants for pure uranium have not been reported undoubtedly due to the difficulty in preparing suitable single crystals and the complexity of the determinations for low symmetry phases. Thus, theoretical calculations of the kinetic features similar to those made by Knapp and Dehlinger (14) for iron-carbon alloys are not presently possible. Furthermore, the lattice parameters of the three allotropic phases at the transformation temperatures were not reported, therefore precluding calculation of the crystallographic features by theories similar to that of Lieberman, Wechsler, and Read (25, 26).

The lattice parameters of the phases at the transformation temperatures are now available as the result of the present investigation. In addition experimental data contributing to the description of the general features and kinetics of the allotropic transformations in uranium will be presented.

MATERIALS

The materials used in the course of the investigations conducted were two grades of high-purity uranium and crystal-bar zirconium. The zirconium was used to prepare uranium-zirconium alloys for the determination of the lattice parameters of gamma uranium. "Ames Biscuit" uranium, containing about 500 ppm total impurity, was used in preparing the uranium-zirconium alloys. The uranium used for all other experiments was high purity metal obtained from the General Electric Company's Hanford Works. Their analysis for the impurities in this material is given in Table 1.

Table 1. Analytical results for impurities in the high-grade uranium used in these investigations

Impurity	Impurity concentration (parts per million)
C	35
H	4
Al	20
Cr	2
Fe	18
Mg	5
Mn	10
Ni	10
Pb	5
Si	22

APPARATUS AND PROCEDURES

Measurement of the Electrical Resistance and Sonic Activity of Bar Samples

The effect of thermal cycling uranium bars through the transformations on their resistance and alpha phase sonic activity was studied employing the techniques described below.

An alternating current poteniometric method for the measurement of the electrical resistance was used. The apparatus including furnace and automatic recording and control instruments has been described in detail by Chiotti (27). In this apparatus the sample in the form of a bar is clamped between two water-cooled copper electrodes and is heated by passing a 60-cycle alternating current through it. The resistance is measured by balancing the potential developed across a central portion of the sample against a potential developed across the secondary of a current transformer. The primary of the current transformer is connected in series with the test bar. Consequently, the reading of the potentiometer is directly proportional to the resistance of the sample. A continuous record of the electrical resistance was obtained by means of an automatic recording potentiometer.

The samples used in this investigation were high-purity uranium bars 5 inches long of 3/16 inch square cross-section. The bars were mounted between copper electrodes with one end rigidly attached to one electrode. The other end made a

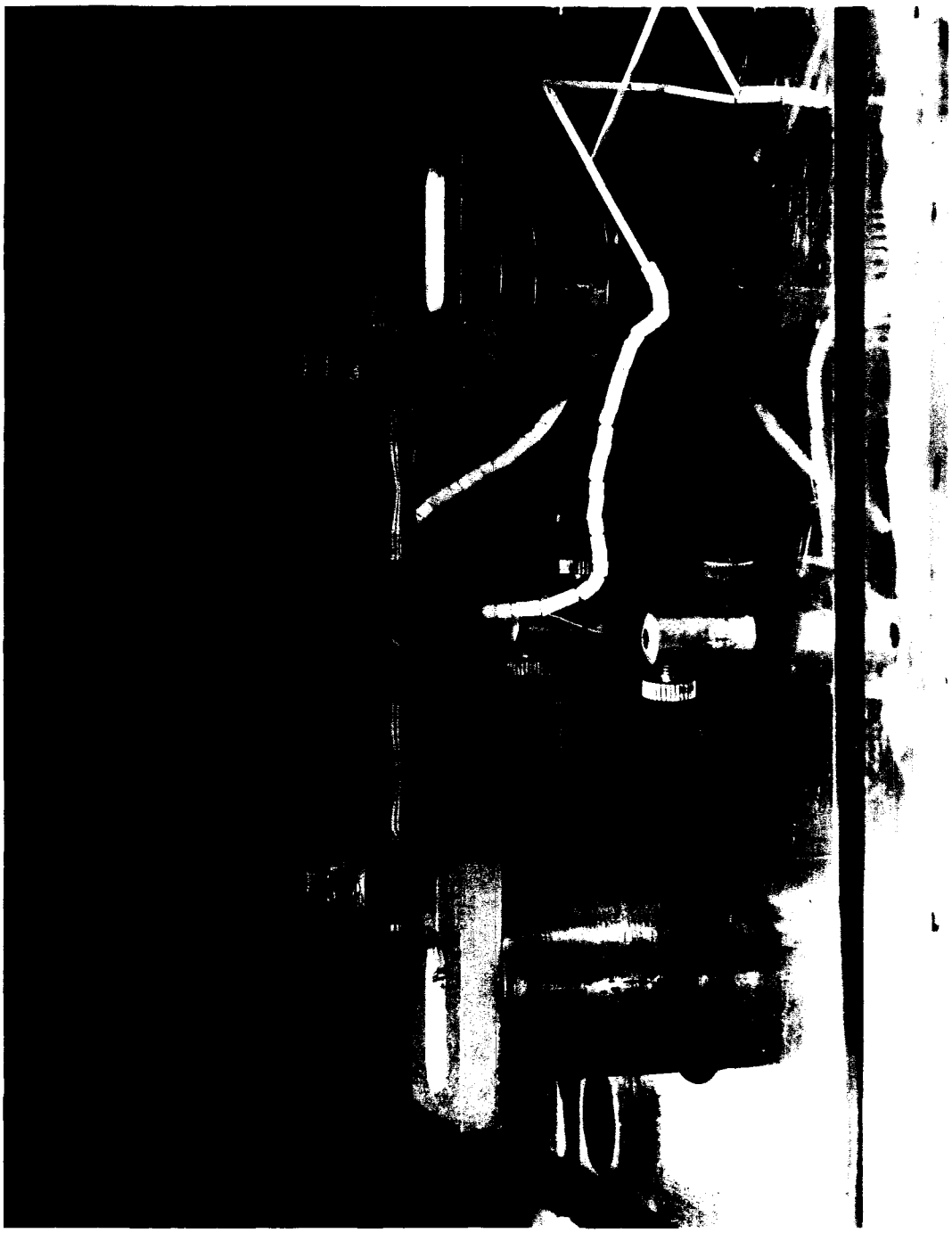
sliding contact on the second electrode. Electrical contact at the free end of the bar was supplemented through a flexible copper cable and clamp. A Pt/Pt-13%Rh thermocouple was spot welded to the center of the bar. Two tantalum probes spaced about 5/8 inch apart were spot welded to the bar at a position near its midpoint where the temperature was quite uniform. A uniform temperature region between the probes was obtained by reducing the cross-sectional area of the bar between the probes and the electrodes. The experiments were carried out at pressures of less than 10^{-5}mm of Hg.

Thermal cycling was accomplished by manually switching the power to the bars between predetermined levels. In this manner the rate of cycling and the temperature range of the cycles were easily varied for various investigations. The temperature and resistance of the bar was continuously recorded during the cycling. A Bristol high speed recording potentiometer was employed for the temperature record.

When sonic activity was also to be detected, the bar samples were reduced to 1 inch in length and provided with extension current leads made from 1/4 inch tantalum rod. Such leads, 2 inches long, were threaded into the ends of the uranium. Resistivity probes and a thermocouple were spot welded to the uranium between the tantalum-uranium junctions. This assembly was mounted in the resistance apparatus in the same manner as were the 5 inch bars. A sample of this type is shown mounted in the apparatus in Figure 1. The tempera-

Figure 1. Uranium sample for resistance and sonic experiments shown mounted (center) in alternating-current resistance apparatus

Spot welded to the uranium are thermocouple wires (insulated with refractory beads) and tantalum wire resistance probes. Sonic pick-up cartridge is taped to the left copper electrode under base plate (out of sight).



ture distribution across the uranium was adjusted by shaping the tantalum leads until all of the metal between the probes was at a constant temperature to within about $\pm$ 10°C. Since tantalum does not exhibit sonic activity, this arrangement restricted the sonic activity to that arising from a uranium specimen of uniform temperature. The copper electrodes to which the test bars were fastened extend through the base of the vacuum chamber.

A piezoelectric phonograph pickup cartridge was taped to one of the electrodes at a point just outside the vacuum chamber. The electrode chosen was that to which the sample bar was rigidly attached. The signal from the cartridge was amplified with a high-gain audio amplifier modified with a 60-cycle filter. The signal was made sensible by a 6 inch speaker. The operation of this arrangement was checked by mechanically stressing a specimen clamped in the apparatus. Clear detection of the "clicks" accompanying the mechanical twinning of either zirconium or uranium at room temperature was possible. The sonic activity associated with the martensitic transformation in a bar of hardenable tool steel was also detected.

During thermal cycling of the uranium bars, sonic activity was recorded by making a pencil mark on the time-temperature curves on the recorder chart whenever audible reports were heard. The final data were gathered from the time-temperature and time-resistance recorder chart curves. The time-

temperature curves gave time to ± 0.02 minutes and temperature to ± 2°C; changes in temperature of 1°C being readily observed. Changes in resistance were of primary interest in these studies. The time-resistance curves yielded resistance values to ± 0.05% of the total resistance at the transformation temperatures and time to ± 0.2 minutes.

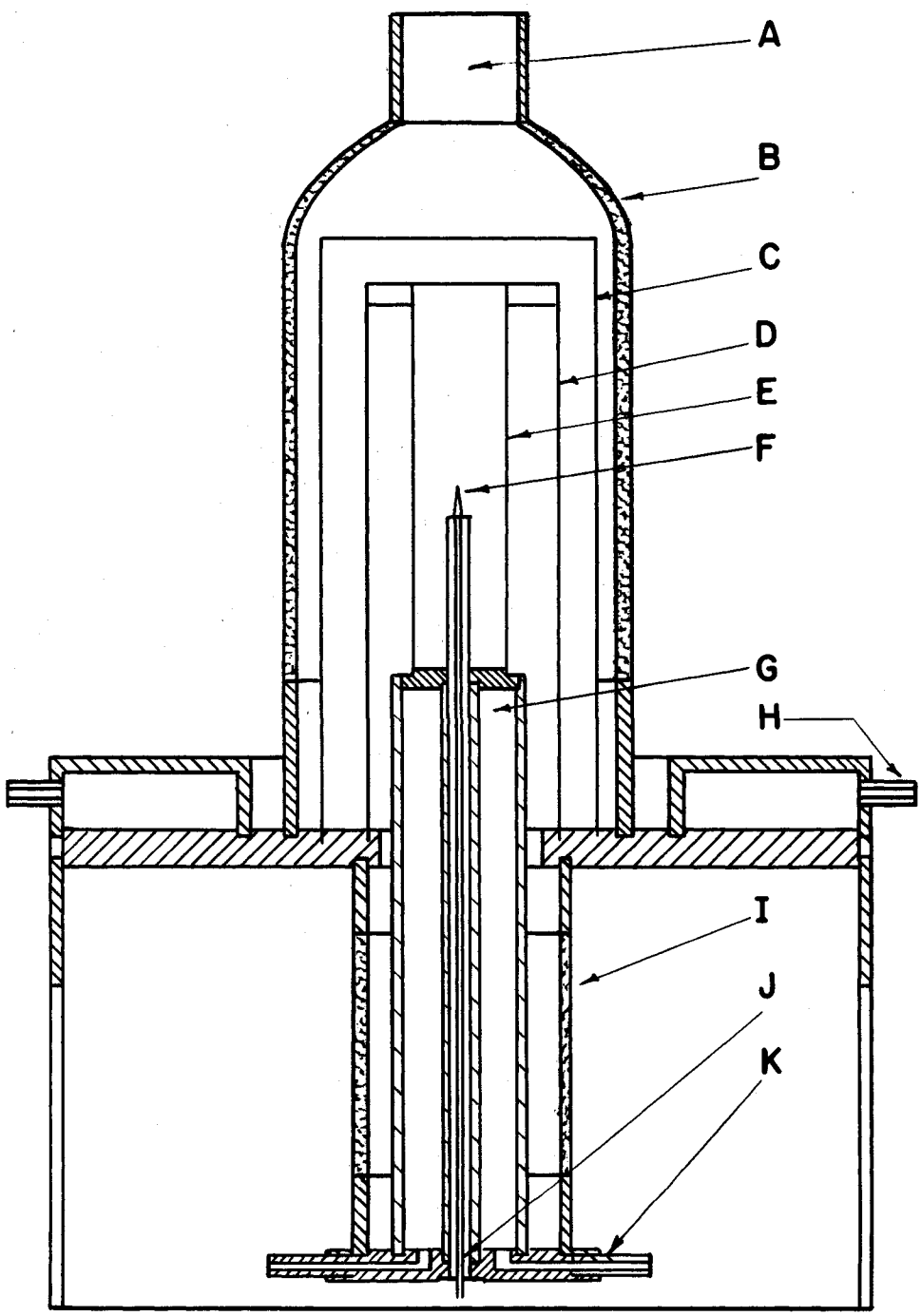
Measurement of the Electrical Resistance of Wire Samples

The isothermal transformation of pure uranium wires was studied. Transformation was detected by observing the change in the resistance of the wires during the formation of a new phase. The wires were heated under vacuum in a small tantalum resistance furnace. A constant, regulated direct current was passed through the samples and the emf drop between tantalum resistance probes spot welded to the wires was measured. Since the current was maintained constant, the change in emf was directly proportional to the change in resistance.

The tube furnace, shown schematically in Figure 2, was mounted vertically on a heavy copper base plate which served as one current electrode. The heating element of the furnace E was a cylinder of 0.0005 inch tantalum foil 5/8 inch in diameter and 4 inches in height. A second concentric cylinder D of 0.020 inch tantalum carried current from the base plate to a tantalum header at the top of the heating element. The bottom of the heating element was spot welded to a second

Figure 2. Tantalum resistance furnace for wire coil samples

A. Kovar metal ring for receiving sample assembly
B. Glass vacuum bell
C. Tantalum radiation shield
D. Tantalum current lead and radiation shield
E. Tantalum heating element, 5/8 inch diameter, 4 inches high
F. Chromel-Alumel thermocouple
G. Water-cooled electrode
H. Inlet to cooling jacket for base electrode
I. Glass insulator
J. Stupakoff glass-to-metal seal
K. Inlet for cooling water for electrode G


A
B
C
D
E
F
G
H
I
J
K

water-cooled electrode G which was coaxial with the heating element E. This electrode was electrically insulated from the base plate. The electrode had a 1/8 inch pipe running through its entire length which contained an insulated chromel-alumel thermocouple. The termocouple F entered the pipe through a Stupakoff seal J and extended beyond the top of the electrode up to the center of the heating element. A cylindrical radiation shield C surrounded the furnace. The furnace and radiation shield were enclosed by a vacuum bell B. This bell was a glass tube with glass-to-Kovar metal seals at each end. The Kovar ring A of the top glass-to-metal seal received the sample assembly. The vacuum chamber was evacuated, through a glass side arm not shown in the diagram, to below 10^{-5} mm of Hg by a mercury diffusion pump. Power to the furnace was supplied through a step-down transformer whose input could be varied by both coarse and fine autotransformer (powerstat) controls. Approximately 80 amperes were required to bring the temperature in the furnace to 800°C.

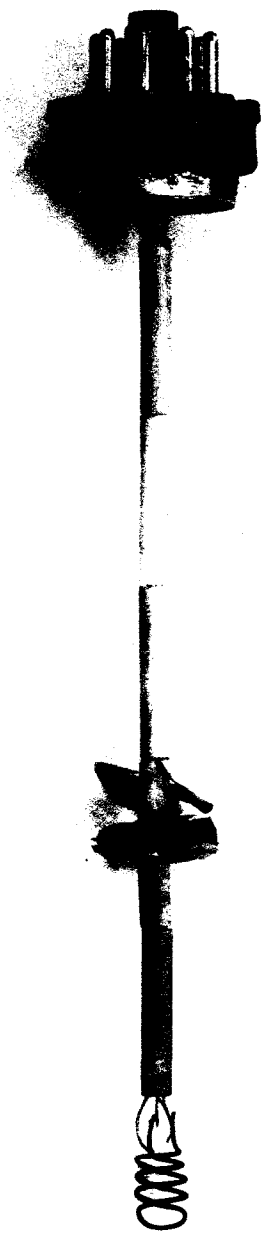
The 0.025 inch uranium wire used was cold-swaged from 3/16 inch bars with one intermediate vacuum anneal at 600°C after reduction to 0.100 inch. The samples studied were made of this wire in the form of non-inductively wound coils 1/8 inch in diameter and 1/2 inch in length. To these coils were spot welded tantalum current and resistivity leads. The length of wire between the resistivity leads was about 3 inches. These leads were passed through a four hole "spaghetti"

insulator and in turn were spot welded to four of the element leads on the octal base of a dismantled metal radio tube. Enough of the metal case of the tube was left in dismantling to make a solder connection to the top Kovar ring, A. The sample assembly is shown in Figure 3. This assembly was arranged so that when the tube base was soldered to the Kovar ring, the uranium coil was located at the center of the furnace with the termocouple junction at its center. Disks of tantalum foil located above as well as below the sample served as radiation shields.

The current to the sample was provided by a constant direct current supply. Controlled currents of approximately 50, 100, 150, and 200 milliamperes were available. The current supplied was found to be constant within 0.01% over the period of time involved in the isothermal experiments. Such a variation is calculated to give an emf change across the samples used of 0.001 millivolts, which is below the variation detectable with even the sensitive recording potentiometer used.

The emf across the samples was recorded with a Bristol high-speed recording potentiometer. A chart speed of 2 inches per minute and a full scale span of 3 millivolts were employed. This arrangement permitted measurement of time to $\pm$ 0.02 minutes and changes in emf drop to $\pm$ 0.005 millivolts. For the samples used and the currents employed, 100 or 150 milliamperes, an emf change of $\pm$ 0.005 millivolts corresponds to a

Figure 3. Sample assembly for resistance measurements on uranium wire coils consisting of: octal base of dismantled radio tube (top), current and resistance probe leads, radiation shields shown on 4-hole refractory insulators (middle), and non-inductively wound coil 1/8 inch in diameter and 1/2 inch in height of 0.025 inch wire



change in total resistance of about 0.05% at the transformation temperatures. A change of about 3.5 - 4.0% in the total resistance of the samples was found to accompany the allotropic transformations.

Temperature was measured with the chromel-alumel thermocouple mentioned using an ice bath cold junction and a Rubicon student potentiometer. Absolute measurement of temperature is estimated to be within 2°C. Changes in temperature could be detected to about 0.5°C.

The isothermal transformation experiments were performed as follows. The samples were first held at some temperature 50 to 100°C from the approximate transformation temperature. They were then cooled or heated to some temperature in the transformation region. This predetermined temperature was then maintained constant while any resistance changes taking place were continuously recorded. It was found possible to cool or heat and fix the temperature in less than a minute. The temperature was maintained constant to within at least $\pm$ 0.5°C during the isothermal transformation studies. Temperature control was obtained by manually adjusting the fine power control to the furnace as necessary to keep the Rubicon potentiometer balanced at a predetermined setting. Attention was given to frequent standardizations of the potentiometer against its standard cell.

Kinetic data at various temperatures were obtained from the analysis of the time-resistance curves. The assumption

was made that the percent metal transformed at any given time was given by the percent resistance change based on the total resistance change accompanying the complete transformation. This assumption will be explored further in the discussion of the results of these experiments.

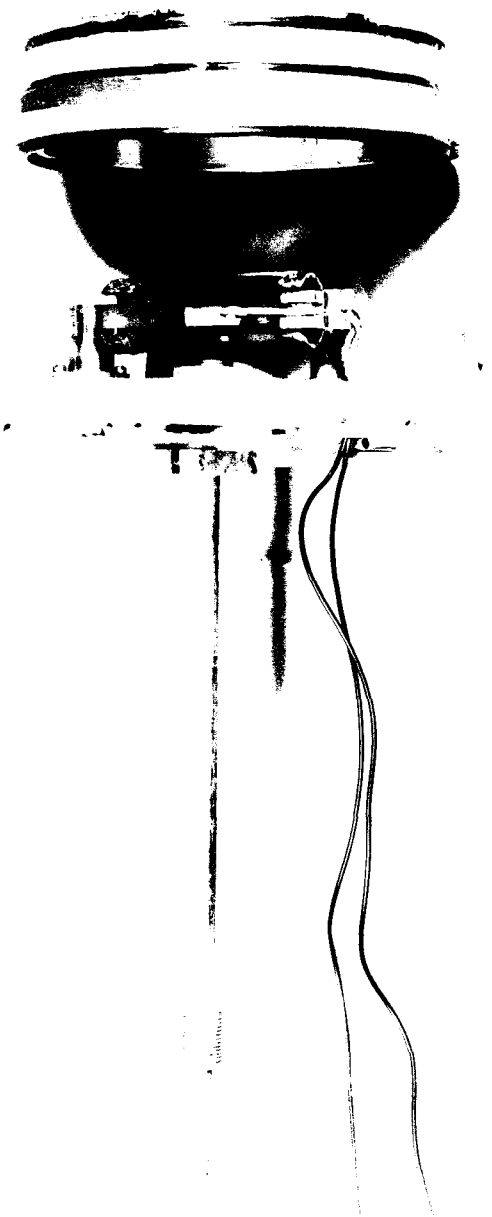
High-Temperature X-ray Determination of Lattice Parameters

The lattice parameters of the three allotropic forms of uranium were determined as a function of temperature. The apparatus used was a Geiger-counter x-ray diffractometer adapted for high-temperature investigations. Discussion of this instrument and construction details of the specimen holder, furnace, and vacuum chamber are given by Chiotti (28). The essential features of the camera can be seen in Figure 4.

The x-ray beam enters and diffracted rays leave the vacuum chamber through a 0.0025 inch aluminum foil window. Essential to the furance is a boat-shaped tantalum resistance element which heats the specimen holder and sample by radiation. Appropriate power leads and radiation shielding complete the furnace assembly. Massive high-purity uranium samples 3/4 inch by 1/4 inch by 1/16 inch were employed. The samples were supported on a tantalum specimen holder.

A Pt/Pt-13% Rh thermocouple was spot welded to the surface of the sample immediately after it had been cleaned by polishing with MgO or etching with dilute nitric acid. The

Figure 4. Top view of high-temperature x-ray diffraction camera showing vacuum cover (right), rectangular sample with thermocouple spot welded to its surface (center), furnace (surrounding sample) attached to water-cooled back plate which mounts in Norelco Gieger-counter diffractometer (not shown)



diffractometer vacuum cover was immediately put in place and the system pumped down. Keeping the time of exposure of the cleaned sample to atmospheric gases to a minimum was considered advantageous relative to surface contamination by oxide and/or nitride.

The determination of lattice parameters above about 400°C was complicated by surface contamination by UO_2 and UC. It was found necessary to make all runs at pressures below 10^{-5} mm of Hg. Satisfactory alpha data were taken at pressures of 2×10^{-6} mm of Hg which were obtained in the system with little difficulty at these lower temperatures. The combination of surface contamination and excessive orientation due to grain growth led to the use of special procedures to obtain the desired information in the beta and gamma regions. The installation of an electronic high-vacuum pump, developed by Consolidated Vacuum Corporation, permitted work in the 700°C to 800°C region at pressures below 8×10^{-7} mm of Hg. Oxide and carbide contamination was still troublesome but not prohibitive. In order to decrease orientation and contamination difficulties in the gamma region, uranium-zirconium alloys, which form a complete series of body centered cubic solid solutions above 800°C, were employed. These alloys were prepared by arc-melting techniques. The desired constants for pure uranium were obtained by extrapolation and were checked by two determinations employing unalloyed uranium.

Copper K_α radiation was employed throughout the investi-

gation and the value λ_{α_1} = 1.5405 A was used. Patterns were recorded at scanning speeds of 1/4 and 1 degree 2θ per minute over a range from 20 to 150 degrees 2θ. The Nelson-Riley (29) graphical extrapolation had been shown by experience with a silicon standard and with thorium to be satisfactory for the determination of refined lattice parameters for cubic phases. In this work it was used to obtain refined values for UO_2, UC, and the body centered cubic gamma uranium. The analytical treatment of the diffractometer data for the parameters of the tetragonal beta and orthorhombic alpha phases demanded special methods.

Cohen's (30, 31) analytical treatment of x-ray diffraction errors is applicable to tetragonal and orthorhombic lattices, but as originally developed the method applies only to reflections for which the Bragg angle is greater than 60 degrees. The back reflection peaks necessary for the extrapolation are simply not recorded above about 400°C. The absence of measurable back reflection peaks is believed to be in a large part due to the attenuation of the intensity with increasing thermal vibration. This effect is expected to be most pronounced for high angle reflections. A modification of Cohen's treatment was therefore developed.

The geometry of the high-temperature diffractometer and the experimental samples used were considered. It was assumed that all systematic camera errors except the eccentricity error could be neglected. This error arises from the dis-

placement of the sample from the rotation axis of the camera. The error in the measured inter planar spacing d resulting from this displacement was derived to be given by the relationship

$$\frac{\Delta d}{d} = - \frac{D}{R} \frac{\cos^2 \theta}{\sin \theta} \qquad 2.$$

where D is the displacement from the rotation axis, R is the distance from the focal spot of the x-ray tube target to the axis of rotation of the camera, and θ is the Bragg angle. It follows from the Bragg equation

$$n\lambda = 2d \sin \theta \qquad 3.$$

that

$$\Delta d = K \left(\frac{1}{\sin^2 \theta} - 1\right) \qquad 4.$$

where K is a constant for any given experimental sample displacement. An equivalent expression was derived by Wilson (32). Empirically a plot of Δd versus $\left(\frac{1}{\sin^2 \theta} - 1\right)$ for samples of cubic materials purposely displaced in the camera extropolated to zero error.

The correction for systematic camera errors to be made in the Cohen analytical extropolation is a correction in $\sin^2 \theta$ of the form

$$\Delta \sin^2 \theta = K \delta \qquad 5.$$

where K is a constant. Starting with the Bragg equation, Equation 3, squaring both sides, taking logs of both sides, differentiating, and assuming

$$\frac{\Delta\lambda}{\lambda} = 0$$

we have

$$-1/2\ \frac{\Delta \sin^2\theta}{\sin^2\theta} = \frac{\Delta d}{d} \qquad 6.$$

Substituting for the right-hand side of this equation from Equation 2, the desired expression is

$$\Delta \sin^2\theta = 2\ \frac{D}{R} \cos^2\theta \sin\theta \qquad 7.$$

where 2 D/R corresponds to the constant K in Equation 5 and the error term δ correspond to $\cos^2\theta \sin\theta$.

Refinements using this error term in the Cohen treatment of the x-ray data give values for the room temperature lattice parameters of alpha uranium in good agreement with the values determined by other methods. The overall precision of determinations of the alpha and beta constants at a given temperature was found to be 0.05% to 0.10%. It is to be noted that in most cases fewer than 20 reflections could be recorded and that these reflections were at Bragg angles less than about 60 degrees.

RESULTS AND INTERPRETATION OF RESULTS

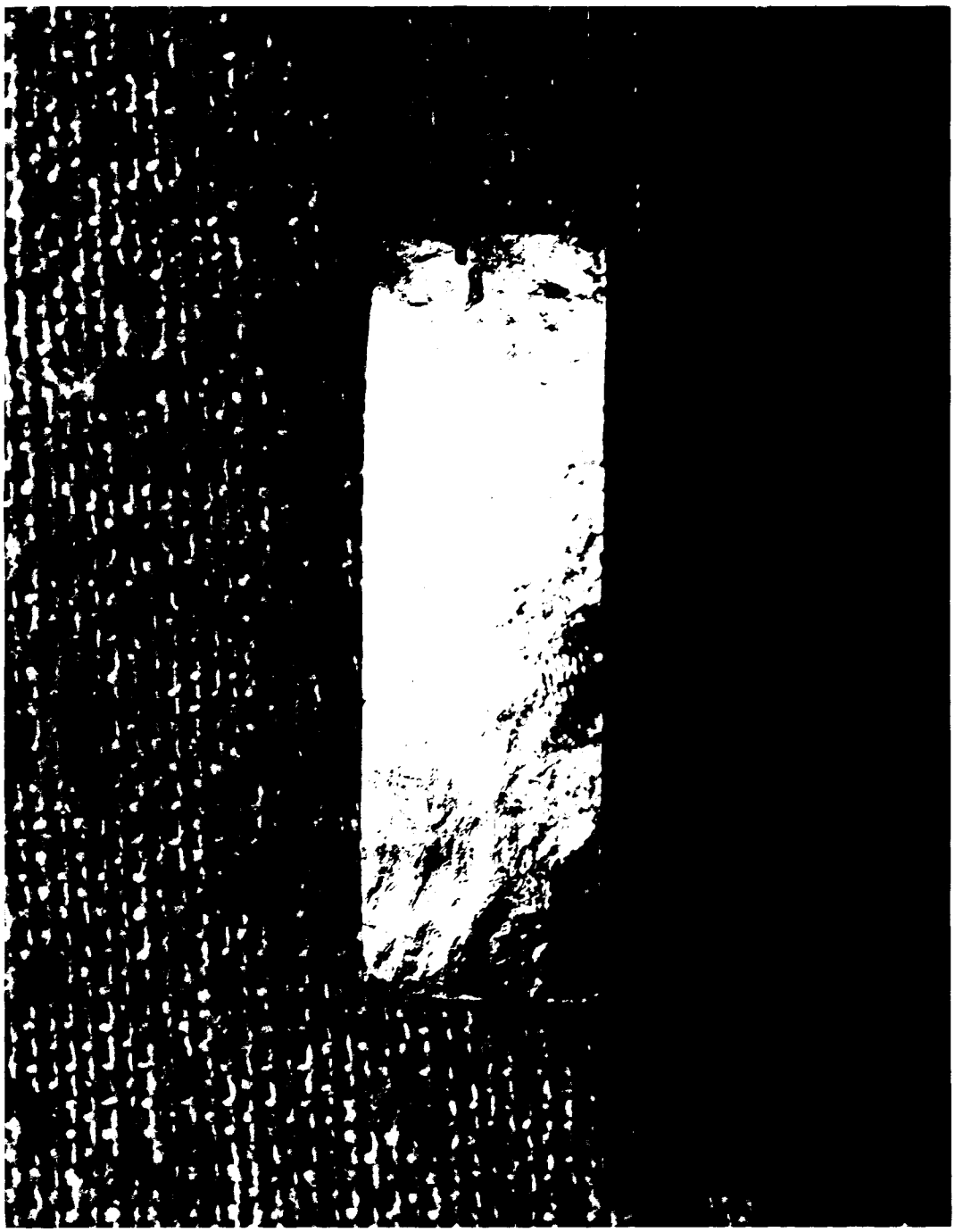
General Features of the Transformations

Surface relief and macroscopic distortions

When metals or alloys undergo a change of crystal structure by a process involving the formation and growth of coherent nuclei, characteristic surface relief effects are commonly observed. These effects are associated with the shear of adjacent regions which is necessary to accommodate the volume changes involved if coherence is to be maintained.

After the transformation of uranium, surface effects were observed as is shown in Figure 5. The surface shown was initially polished and etched. This sample was a specimen used for the determination of the lattice constants of beta uranium. It was heated slowly to above 700°C, held below 770°C for several hours while x-ray patterns were recorded, and then cooled to room temperature in 20 minutes. Similar effects were observed on the surfaces of all samples heated into the beta and gamma regions. However, similar roughening was also observed on the surface of samples thermally cycled between 600°C and room temperature without ever undergoing transformation. Surface roughening and even gross distortion of uranium samples cycled in the alpha region have been observed by many investigators (6) and treated theoretically by others (33, 34). This effect precludes the use of surface relief effects

Figure 5. Surface roughening on 3/4 inch by 1/4 inch by 1/16 inch uranium sample after heating to about 750°C (oblique lighting)



observed at room temperature in studying the nature of the allotropic transformations.

Thermal cycling of the high purity uranium bars in the resistivity apparatus through the transformations resulted in the gross macroscopic distortion and warping demonstrated in Figure 6. An extreme case, indicating the magnitude of the distortions involved, was the observation of the "growth" of a small, electrolytically deposited, uranium bicrystal by approximately 100% in the long direction during an accidental, rapid beta-alpha-beta-alpha cycle. This crystal was mounted on a tantalum wire in an evacuated silica capsule.

These macroscopic distortions were not studied quantitatively in any detail, but are reported as one of the features of the transformations. They were considered in the execution and interpretation of the other experiments performed.

Preferred orientation effects and reversibility

The resistance of each 0.025 inch uranium wire sample over the temperature range from 600°C to 800°C during as many as 20 varied heating and cooling programs was found to be reproducible (with the exception mentioned below) to $\pm$ 0.5% at any given temperature excluding the transformation regions. This statement holds for heating and cooling rates from 2-3°C per minute to a maximum of about 100°C per minute. The resistance changes observed on transformation were 3.5 $\pm$ 1% and 4.0 $\pm$ 1% for the alpha-beta and beta-gamma transformations

Figure 6. Distortion of uranium resistance bars due to thermal cycling through the transformations

A. Original bar metal not cycled (5 inches long and 3/16 inch square cross-section)
B. Cycled bar, necked-down sections were machined prior to cycling to give uniform temperature region in center of the bar
C. Cycled bar showing warping
D. Cycled sonic and resistance sample (1 inch long)


A
B
C
D

respectively.

However, in the case of the uranium bar samples the resistance at any given temperature was not found to be as reproducible, presumably due to the macroscopic distortions described in the previous section. In this case the magnitude of the distortion compared to the resistance probe spacing, 5/8 inch, was not negligible. However, the percentage resistance changes accompanying the alpha-beta and beta-gamma transformations during continuous cycling of a bar at 1/4 cycle per minute between 575°C and 925°C were observed to fall within the range established for the wire specimens, 3.5 ± 1% and 4.0 ± 1%, respectively. That is, the dimensional changes which accompany thermal cycling do not grossly affect the percent change in resistance which results when the metal transforms. When other heating programs were employed, anomalous resistance changes were observed in the alpha-beta transformation, but not in the beta-gamma transformation.

When the cycling of the bar was interrupted to allow the metal to remain for times as short as 9 minutes in the gamma and beta regions or interrupted for this length of time in the beta region alone, the percent change in resistance accompanying the subsequent beta to alpha transformation was either abnormally low, ΔR = 0.5% to 0%, or high, ΔR = 8% to 9%. Resumption of continuous cycling at the previous rate progressively restored the size of the resistance break toward the normal on each 575°C - 925°C - 525°C cycle. Complete return

to the normal 3.5 ± 1% change required two to three such cycles through both transformations. During all of this treatment the size of the beta-gamma breaks remained 4.0% with only the usual 1% scatter. The data presented in Figure 7 for the resistance of a bar sample as a function of temperature shows the effect of a 30 minute anneal in the beta region. It can be seen that in this case not only was the percentage resistance change abnormally low for the beta-alpha transformation, but the temperature of the transformation, if determined by the beginning of the resistance break, was raised about 25°C.

Such abnormally low and high resistance changes through the alpha-beta transformation after beta annealing were not observed in cases where the samples consisted of the coiled uranium wire. It is to be noted that in these cases there was 3 inches of wire between the resistance probes as compared to 5/8 inch in the case of the bars. Figure 8 shows, however, that on the initial heating of these wire samples an abnormally low alpha to beta resistance change was observed. One or two subsequent beta-alpha-beta cycles established the normal 3.5 ± 1% change which was maintained throughout further thermal treatment as stated above.

It is proposed that these effects arise from the establishment of preferred crystallographic orientation in the metal.

Evidence for rapid beta grain growth has been noted in

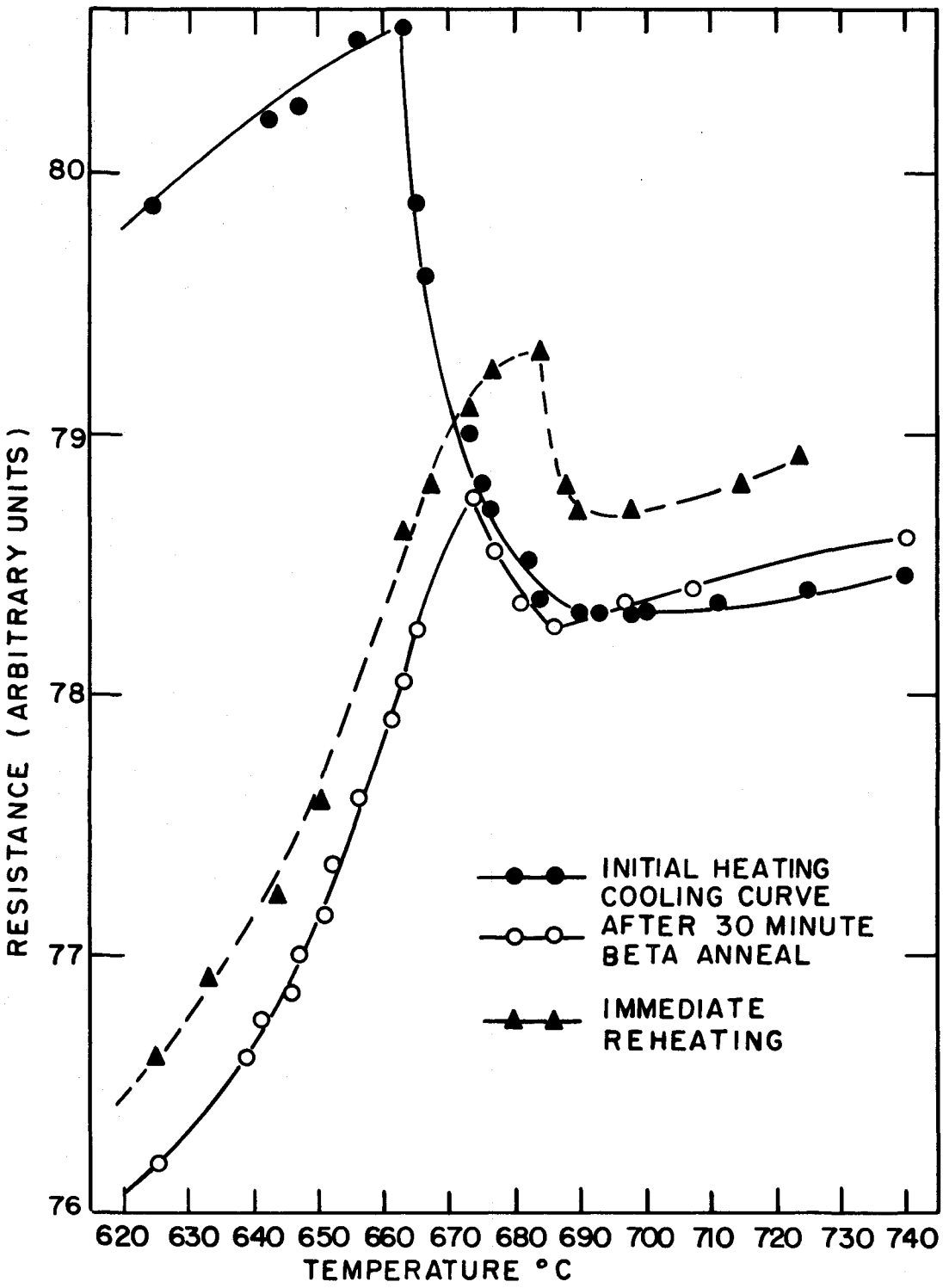


Figure 7. Resistance versus temperature plot for uranium resistance bar in the alpha-beta transformation region showing the effect of a 30 minute beta anneal

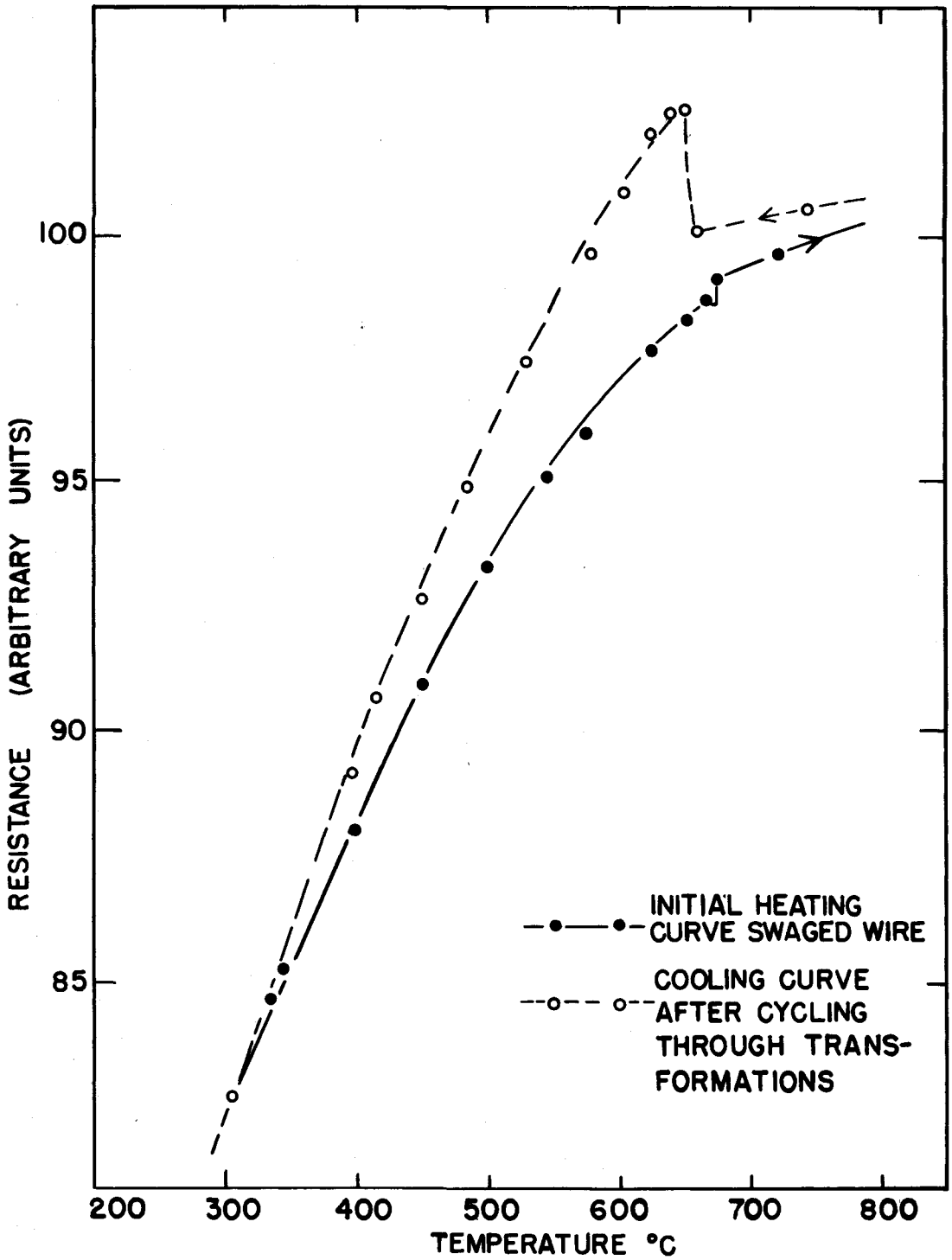


Figure 8. Resistance versus temperature plot for swaged uranium wire sample showing the effect of subsequent cycling on the resistance change at the alpha-beta transformation

the course of the high-temperature x-ray diffractometer studies on the lattice parameters of the beta phase. Some of the reflections recorded when first heating a fine-grained, randomly-oriented sample into the beta region were observed to disappear in only a few minutes while a few others became stronger. These observations can be explained on the basis of grain growth and orientation effects. The preferred orientation in the bar samples undoubtedly arose due to rapid beta grain growth. Since the probe spacing was relatively small compared to the cross-sectional area of the bar, a few large grains would effectively produce a high degree of preferred orientation.

The wire samples used would be expected initially to have a fairly high degree of preferred orientation since they were prepared by swaging. The orientation was evidently randomized by thermal cycling. Subsequent orientation effects due to beta grain growth were minimized by the small diameter and the relatively long length of wire between the resistivity probes. In this case it would be expected that in the absence of any large temperature gradients, approximately equiaxed grains would be formed as a result of recrystallization and grain growth. Hence, one would expect that there would always be a large number of grains between the resistivity probes and that the effective orientation of all of these grains would remain nearly random.

From Tucker's analysis of the bonding in the alpha

structure (2) one expects a large anisotropy of electrical conduction. Thus, oriented beta very probably transforms to give alpha orientations of effective resistance much above or below the random value. This implies that the alpha orientations arising from a given beta orientation are restricted to certain definite relations. This is to be expected on the basis of strain energy considerations if the transformation involves coherent nucleation and growth. It should also be noted that the experimental results indicate no pronounced anisotropy in the electrical resistivity of the beta phase. The resistivity of the cubic gamma phase would, of course, be expected to be isotropic. Therefore, transformation of oriented beta to gamma could not be expected to give rise to very unusual resistance effects.

Due to the reversibility characteristic of a coherent transformation, a highly oriented specimen is expected to retain its preferred orientation to a large extent even on cycling many times through the transformation. This is indeed the case for the zirconium allotropic transformation (35). The observations reported here for uranium indicate that preferred orientation is randomized by cycling, but only progressively over two to three cycles through both transformations. This partial retention of the orientation indicates some degree of reversibility associated with both transformations. Such persistence of orientation would be much more difficult to account for if the transformations involved

incoherent nucleation and growth.

Butcher (24) points out that if the alpha-beta transformation does involve coherent nucleation and growth, randomization in a few cycles is still to be expected due to the polygonization and thermal twinning known to occur during the alpha part of the cycle and to rapid grain growth in the beta part of the cycle. The beta grain growth destroys the strain "memory" in the material into which the grain has grown. Polygonization and twinning obviously fragment the structure.

In conclusion it can be said that anomalous resistance changes have been observed accompanying the alpha-beta allotropic transformation in uranium. When the known structural and metallurgical properties of the three phases are considered, these anomalies indicate a certain degree of reversibility in the orientation of a given grain on cycling through both transformations. Such reversibility is typical of so called martensitic transformations.

Alpha phase lattice hardening on cycling

Processes in solids involving the very rapid cooperative movement of atoms in phase, such as occur in typical martensitic transformations and deformation by twinning, produce sound. This sound may be detected and amplified by electronic methods as described in the section on apparatus and procedures.

On rapid cooling of uranium at rates up to 500°C per

minute no reproducible sonic activity has been detected associated with the allotropic transformations. This does not exclude the possibility that such activity might be observed with a more sensitive apparatus and more rapid rates of cooling. Results reported below on the kinetics of the transformations do imply that no sonic activity is to be expected at least at the cooling rates investigated.

Sonic activity was observed on cooling uranium bars in the alpha region. At cooling rates as low as 50°C per minute sharp metallic "clicks" were heard. The first "clicks" were the loudest. If a bar had not been previously cycled through the transformations, the first activity on cooling from 660°C was detected at 400 ± 10°C. Activity per unit time increased at lower temperatures. No activity in this same temperature region was observed for these bars on heating at any rates available (about 600°C per minute). Little or no activity was detected in these experiments when the uranium was replaced by similar samples of zirconium and of tantalum.

Cahn (8) has also reported sonic activity in the alpha phase. He further demonstrated metallographically that twinning is superceded by slip, kinking, and polygonization as a mode of deformation in uranium above about 400°C. These alpha phase "clicks" are undoubtedly associated with thermal twinning, i.e., twinning to relieve local intergranular stresses arising from the random orientation of grains and the anisotropy of thermal expansion. On reheating, the residual

elastic stresses present in the metal after cooling must be reversed before intergranular stresses of opposite sign can build up again. For this reason, in the 400°C range above room temperature in which twinning is the predominant mode of deformation, the critical intergranular stress for twinning is apparently never reached.

Cycling of uranium bars between 300°C and 700°C fairly rapidly, 3/4 cycle per minute, raised the temperature at which thermal twinning was first detected by the sonic "clicks". Figure 9 shows this effect graphically. This temperature could be increased progressively from 400 ± 10°C to as high as 500°C in only ten such cycles. Cycling through both transformations at about one cycle per minute was even more effective in raising the "thermal twinning temperature". Twinning at temperatures as high as 550 ± 20°C was detected during an extended cycling program involving 100 cycles.

Partial or total recovery of the thermal twinning temperature to 410 ± 10°C after cycling was accomplished by long gamma annealing and slow cooling. Slow cycling in the alpha region was also found to be effective, but not as much so as the gamma anneal.

The rise in the thermal twinning temperature was not the only effect observed during rapid cycling through the transformations. If the rate of cycling of either wire or bar samples was increased to a value greater than about 1/2 cycle per minute, the resistance of the newly-formed alpha was found

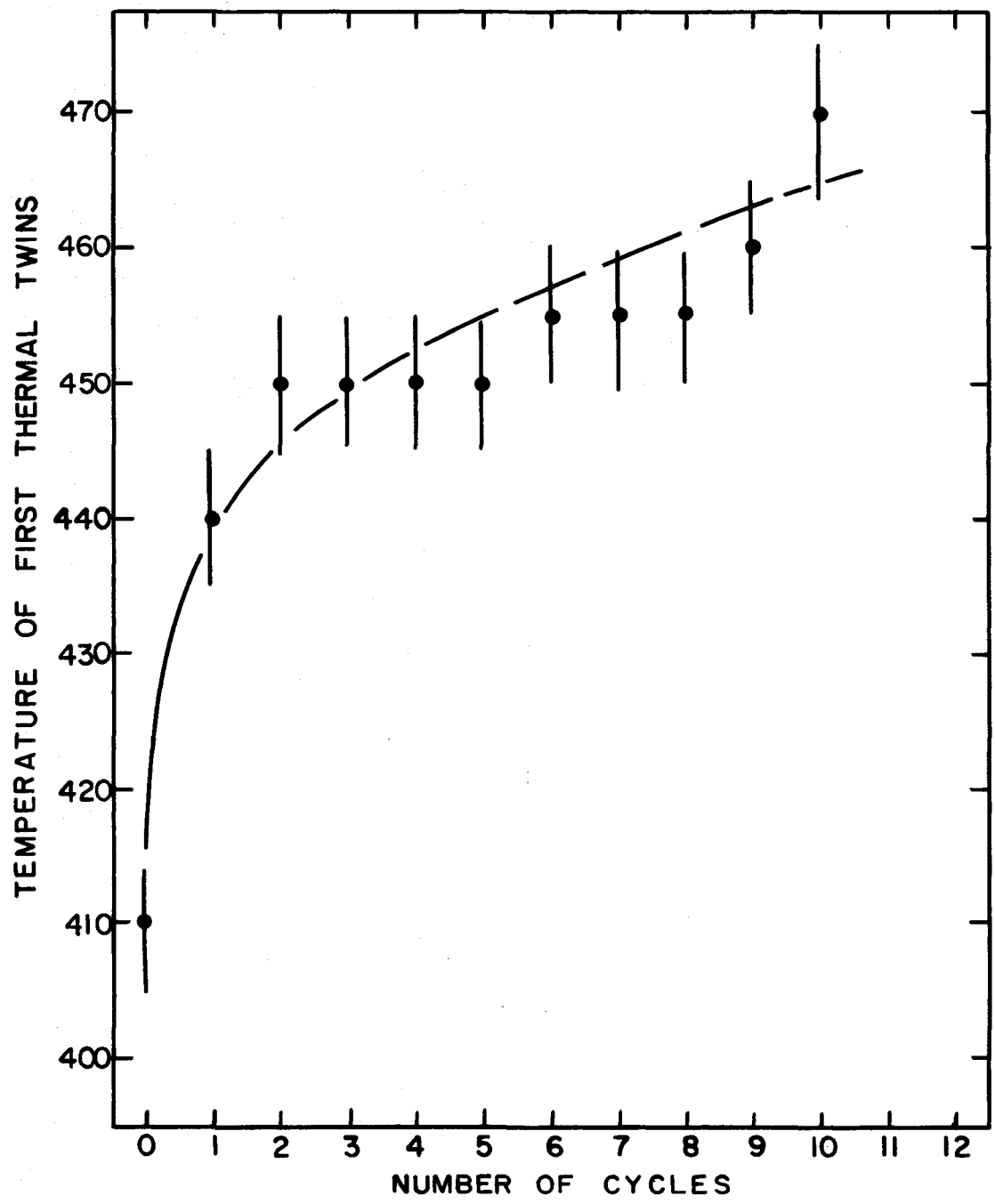


Figure 9. Thermal twinning temperature in alpha uranium versus number of cycles through the alpha-beta transformation (bar sample, sonic detection of twinning)

to be 1.7% to 3.5% higher than normal. The resistance of the other phases on formation varied only within the ± 0.5% limits established for the lower cycling rates. It is to be noted that this was much more rapid cycling than that involved in the studies of preferred orientation and reversibility reported in the previous section. Interruption of the cycling at 600°C just after the formation of alpha was followed by a decrease in resistance toward the normal value.

Furthermore, during a series of six such rapid cycles of a bar sample through both transformations the temperatures of the thermal arrests on cooling at 150°C per minute were progressively lowered. On the sixth cycle the lowering was 6°C for the gamma to beta transformation and 8°C for the beta to alpha transformation.

These effects, the variation of the thermal twinning temperature, the increase in the resistance of the newly-formed alpha phase, and the lowering in the temperature at which the transformations began, which were observed on prolonged rapid cycling are almost certainly due to lattice hardening. The effects of orientation can be excluded since the cycling program employed in this phase of the investigation would be expected to lead to randomization of the crystallites in the metal. It should also be reemphasized that under these conditions randomization does not preclude coherent nucleation and growth even though such a process would tend to preserve any preferred orientation present, as has already been pointed

out.

In general the increase in hardness of metals at any given temperature is related to an increase in the concentration of crystal imperfections in their lattices. Any process which increases the imperfection of the lattice, such as cold working, also increases its hardness and makes deformation by slip more difficult. Whenever the number of slip modes is limited or the degree of imperfection in the lattice is large, deformation by twinning may become an important mode for stress relief. This is particularly true for anisotropic metals such as uranium. The particular modes of deformation which are active, slip or twinning, will, of course, also depend on the temperature.

The observation of a progressive rise in the thermal twinning temperature indicates a definite progressive hardening of the alpha uranium lattice upon cycling through the transformation. Butcher (24) examined uranium metallographically at room temperature after successive alpha-beta-alpha cycles and reported the presence of more twinning after each cycle. He reported this as evidence for lattice hardening. This hardening is presumably due to deformation arising from the transformation distortions.

It is quite clear, as Butcher (24) pointed out, that progressive hardening on cycling through the transformations and in fact any high level of strain in the product phases after complete transformation can hardly be explained if the

transformation takes place by incoherent nucleation and growth. In that event the product phases would essentially be formed as free of imperfection as if they had been completely recrystallized. However, the transfer of crystal imperfections from one lattice to another on cycling through transformations could conceivably be accomplished if the transformations take place by the cooperative movement of a large number of atoms, i.e., by a coherent growth process. Thus, imperfections generated in the alpha phase during an initial beta to alpha transformation in uranium could be retained in the metal throughout a complete cycle through both transformations. They would be added to on the next cycle and so on, presumably until some critical concentration were built up. If cycling were interrupted, some of the imperfections would be removed by annealing processes.

The fact that the resistance of the newly-formed alpha phase is affected more than the beta resistance indicates the greatest share of the deformation involved is taken by the softer alpha phase. Annealing and recrystallization in the gamma phase is expected to be very rapid and may obscure any effect on the resistance due to deformation at the rates of cycling investigated.

The lowering of the thermal arrests on successive cycles evidently means that the presence of an abnormal concentration of imperfections in some way hinders the nucleation and/or growth of the product phases. Since the growth of coherent

nuclei is believed to involve the movement of a dislocation boundary into the parent phase (14), the effect may be very similar to the hardening of metals by cold working. The dislocations already present in the parent matrix could be expected to hinder the movement of the dislocation boundary which is generating the new phase. An alternate possibility, supported by the observed 25°C rise in transformation temperature after a 30 minute beta anneal, is that the lowering is related to the randomization of orientation on cycling. In this case the effect on the transformation temperature of intergranular stress due to anisotropy of thermal expansion should be examined. The effect of external pressure on martensitic transformation temperatures has been given considerable attention (36, 37).

Isothermal-athermal features

Employing wire samples, in which orientation effects were at a minimum, the isothermal resistance changes in the transformation temperature regions were studied. Samples were held at some temperature 50°C to 100°C from the transformation region, cooled or heated rapidly to some predetermined temperature in this region and then held at this latter temperature.

For both transformations on heating (or cooling) a temperature was observed below which (or above which) no transformation took place isothermally in a reasonable period of

time, about 1 hour. Above (or below) this temperature an isothermal change in resistance was observed.

Typical resistance-time curves for both transformations on heating are shown in Figure 10. These isothermal curves on heating exhibited an initial rapid decrease in resistance and then slower decreases to an apparent end of transformation. Upon further heating to a slightly higher temperature, however, the resistance drop began again, continued isothermally, and again stopped. The resistance continued to decrease in this manner upon step-wise heating over a 15°C to 25°C temperature range. It is to be noted that on the isothermal segments of the curves the resistance change was uneven or step-wise in nature. These features were also observed for the alpha to beta transformation of bar samples on the initial heating, in which case complications of large beta grain size did not interfere. The disappearance of an alpha x-ray reflection in the transformation temperature region also showed these general characteristics.

It should be stated at this point that these observations are not believed due to thermal gradients across the samples. The temperature distribution over an entire uranium coil was shown by experimental checks to be constant to within at least 5°C. The range of temperature over which isothermal resistance change was observed was of the order of 15°C to 25°C. Furthermore, this range of temperature was reproducible to within a few degrees for both wire samples and bar samples.

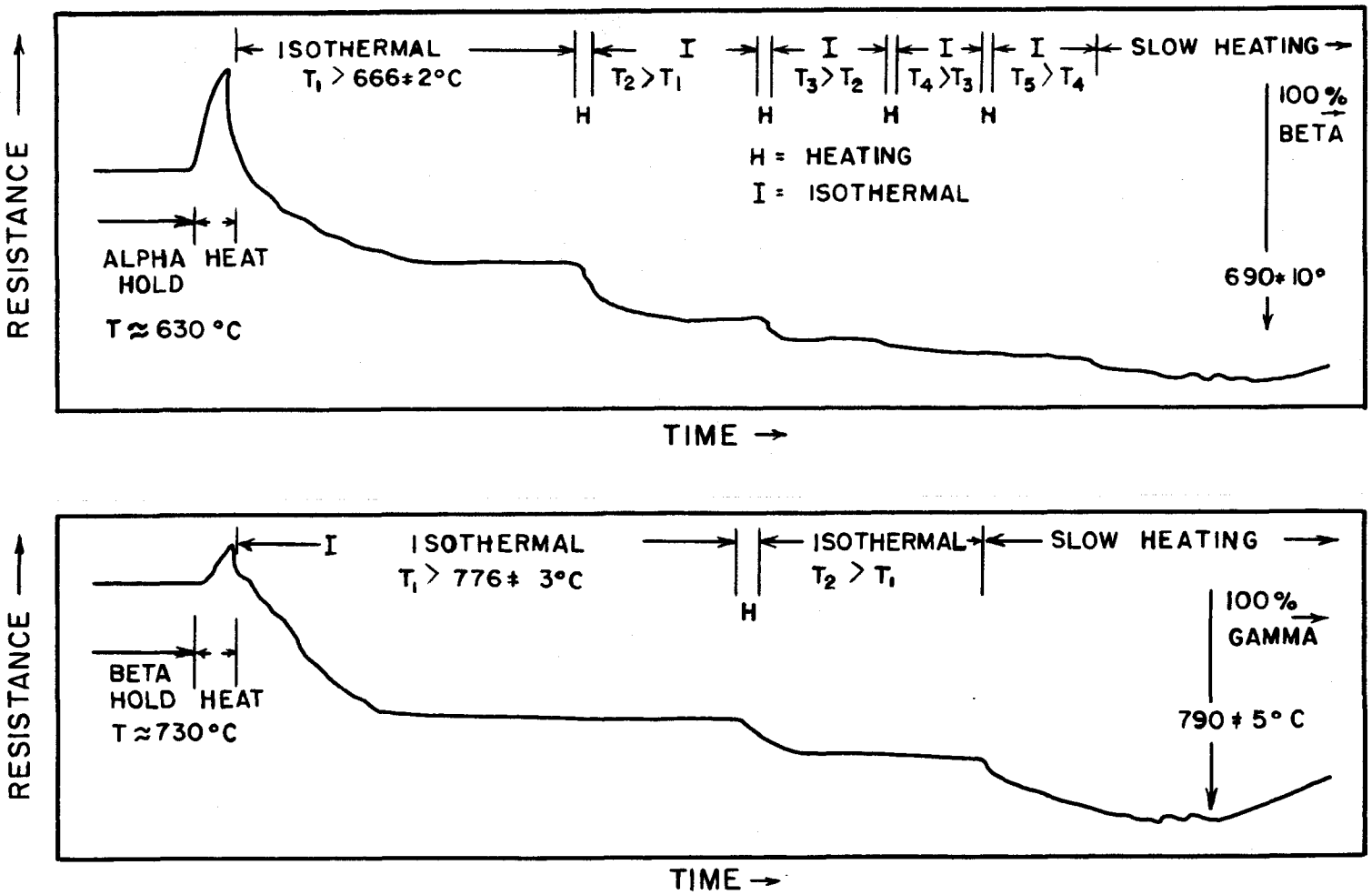


Figure 10. Sketch of the features of resistance-time chart curves for uranium wire samples in the alpha to beta (top) and beta to gamma (bottom) transformation regions on stepwise heating

Considering the wide differences in construction of the two pieces of apparatus used for the measurements on these two types of samples, such agreement due to similar thermal gradients must be considered quite improbable.

Typical isothermal curves for both transformations on cooling are shown in Figure 11. The resistance-time curves for isothermal transformation on cooling were complicated by an initial rapid rise in resistance. This initial rise was followed by some fluctuation prior to a general decrease. The isothermal resistance change then continued to an apparent end of transformation, with the expected rise in resistance. At the start of the regular portion of the curve only 10-30% of the total resistance rise had taken place. Upon further cooling after all isothermal resistance change had apparently stopped, the resistance again began to rise. This rise continued isothermally at some lower temperature and again stopped. This train of events followed on stepwise cooling over about a 15°C range.

The reason for the initial irregular portion of the curves is not known. In part it may be due to recalescence not detected by the thermocouple in the center of the coil and, therefore, not compensated by an appropriate power adjustment. Strain effects and orientation of the new phase relative to the current path might also play a part. One possibility is that the new phase initially forms as thin lenticular plates some of which are perpendicular to the direction of

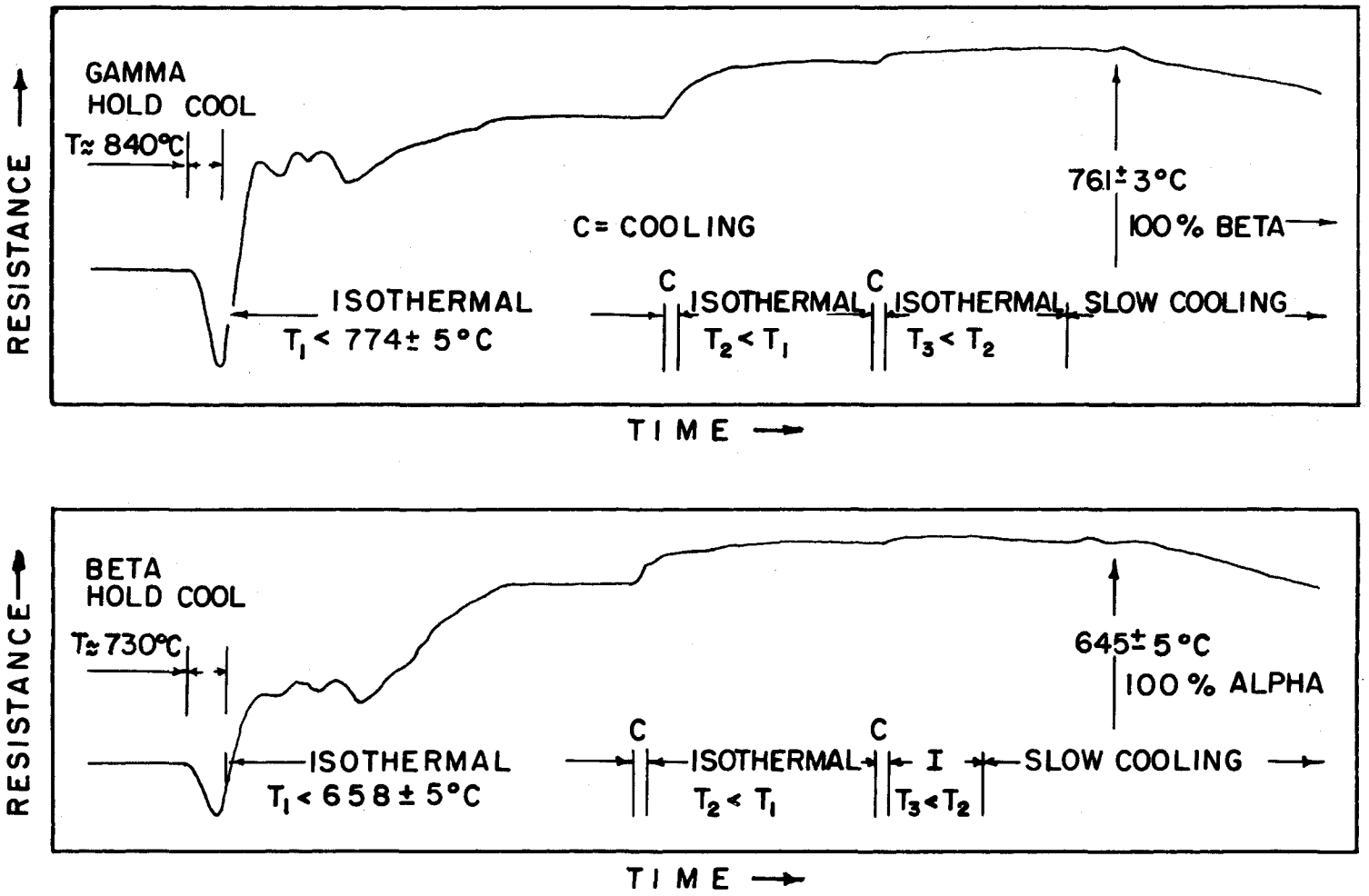


Figure 11. Sketches of the features of resistance-time chart curves for uranium wire samples in the gamma to beta (top) and beta to alpha (bottom) transformation regions on cooling

current flow in the wire. In that case the change in resistance would be greater than that expected for a given volume percent transformed. Subsequent distortion of these platelets might possibly account for the later drop in resistance.

The resistance change at the apparent end of transformation for a given isothermal run was converted to percent transformed by the relation

$$T = \frac{R_a}{R_t} \times 100 \qquad 8.$$

when R_t is the total change in resistance measured for the complete transformation over the 15 to 20°C range, R_a is the resistance change at the apparent end of isothermal transformation, and T is taken to be the volume percent of product formed.

These data as a function of isothermal transformation temperature for the alpha to beta and beta to gamma transformations on heating are presented in Figure 12 and Figure 13. In these figures the open symbols refer to the percent transformed at the apparent end of transformation on first heating to the holding temperature indicated. Solid symbols refer to percent transformed at apparent end of transformation at one of the subsequent temperatures in the step-wise heating process described. Similar data for cooling are shown in Figure 14 and Figure 15.

A nomenclature for the critical temperatures (indicated on the figures by boxes containing crosses) similar to that

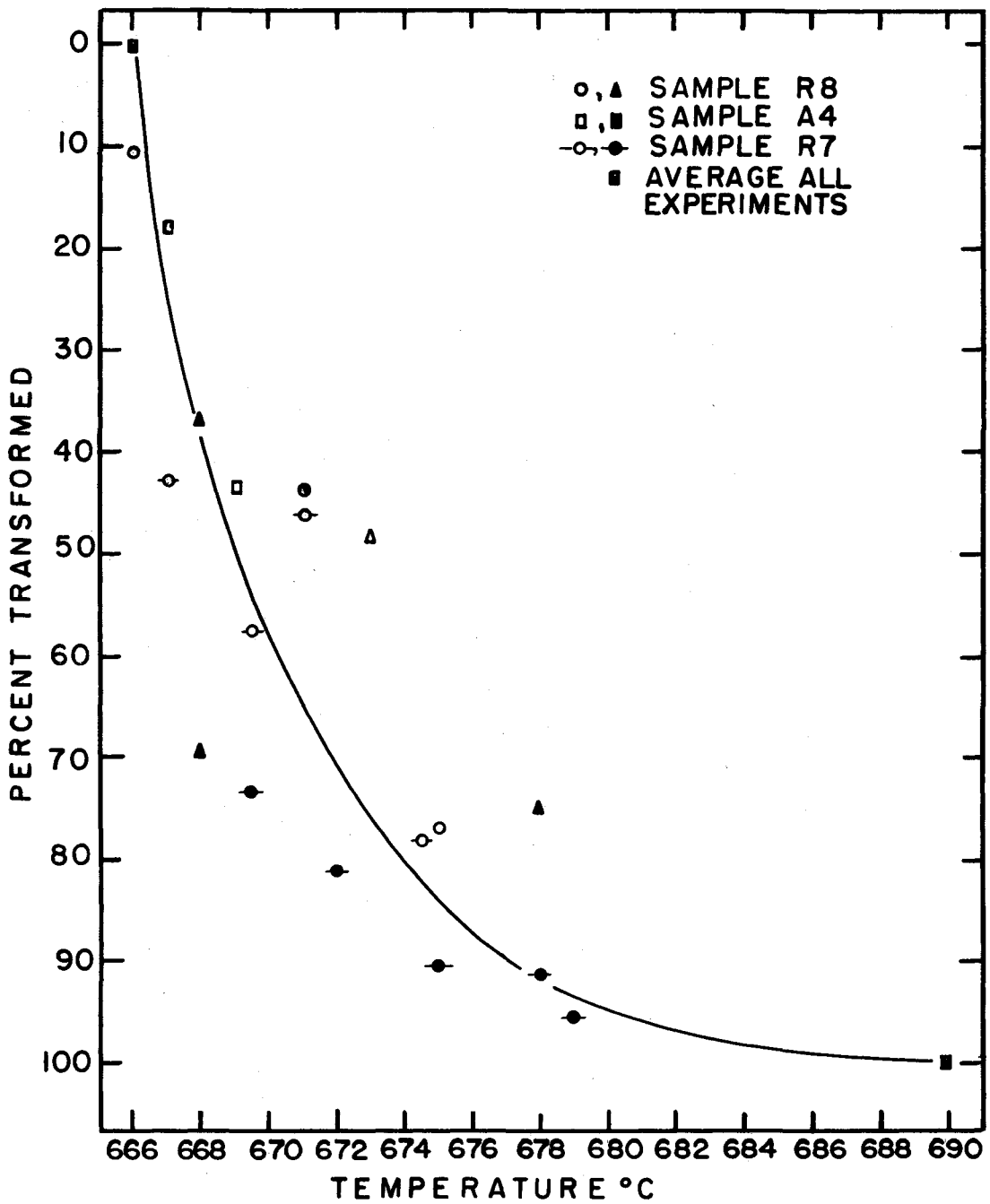


Figure 12. Percent transformed at apparent end of isothermal transformation as a function of temperature for the alpha to beta uranium transformation

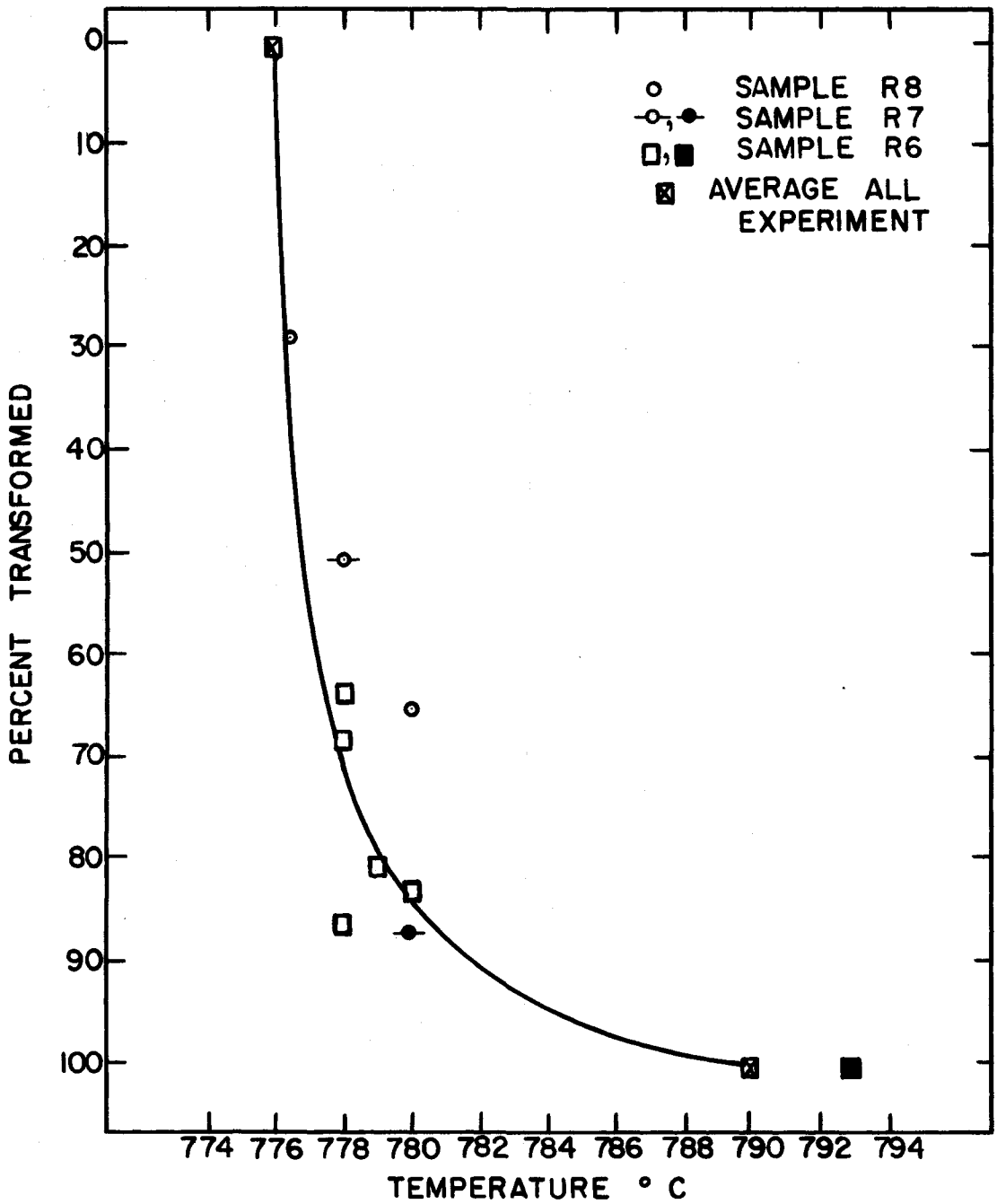


Figure 13. Percent transformed at apparent end of isothermal transformation as a function of temperature for the beta to gamma uranium transformation

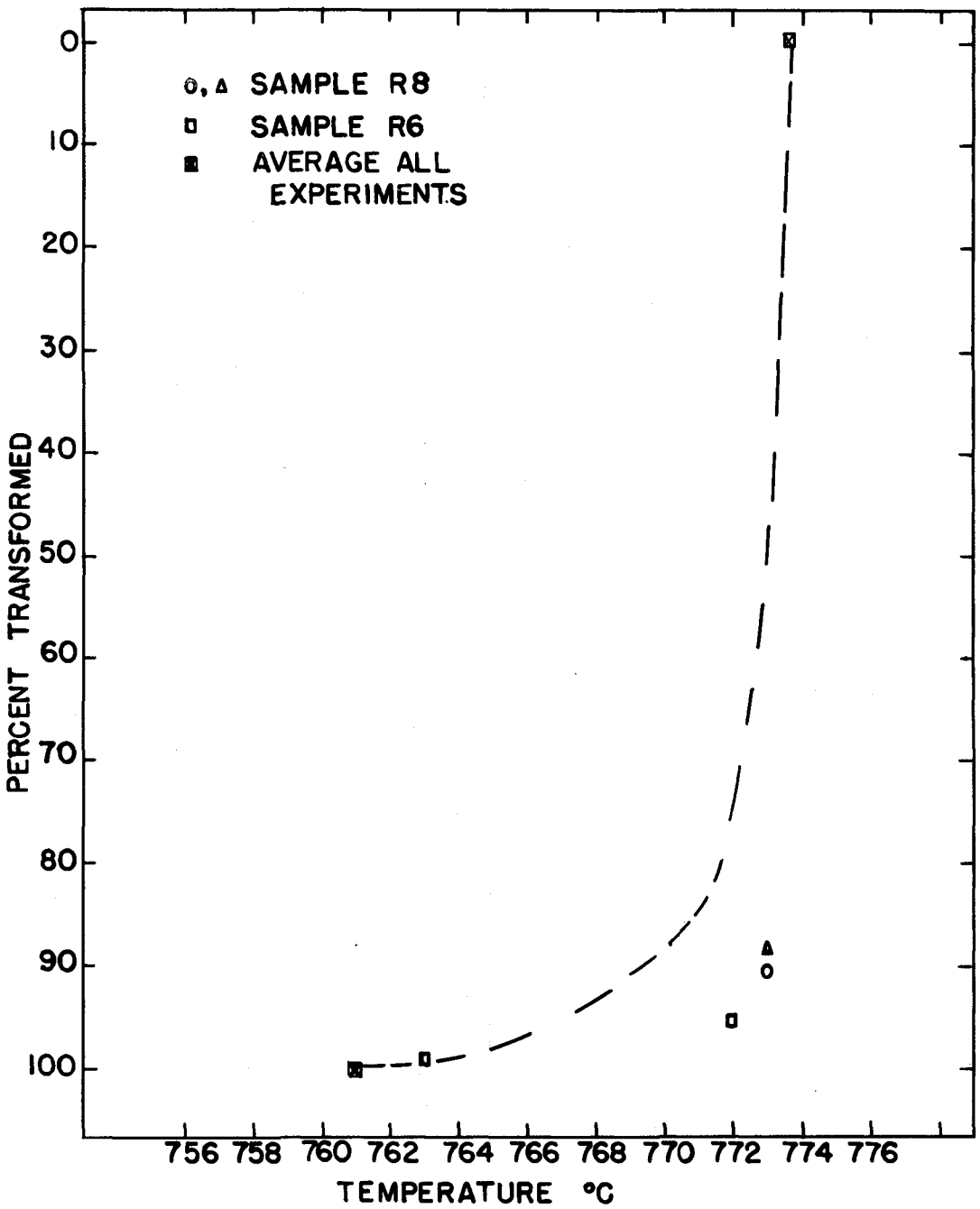


Figure 14. Percent transformed at apparent end of isothermal transformation as a function of temperature for the gamma to beta uranium transformation

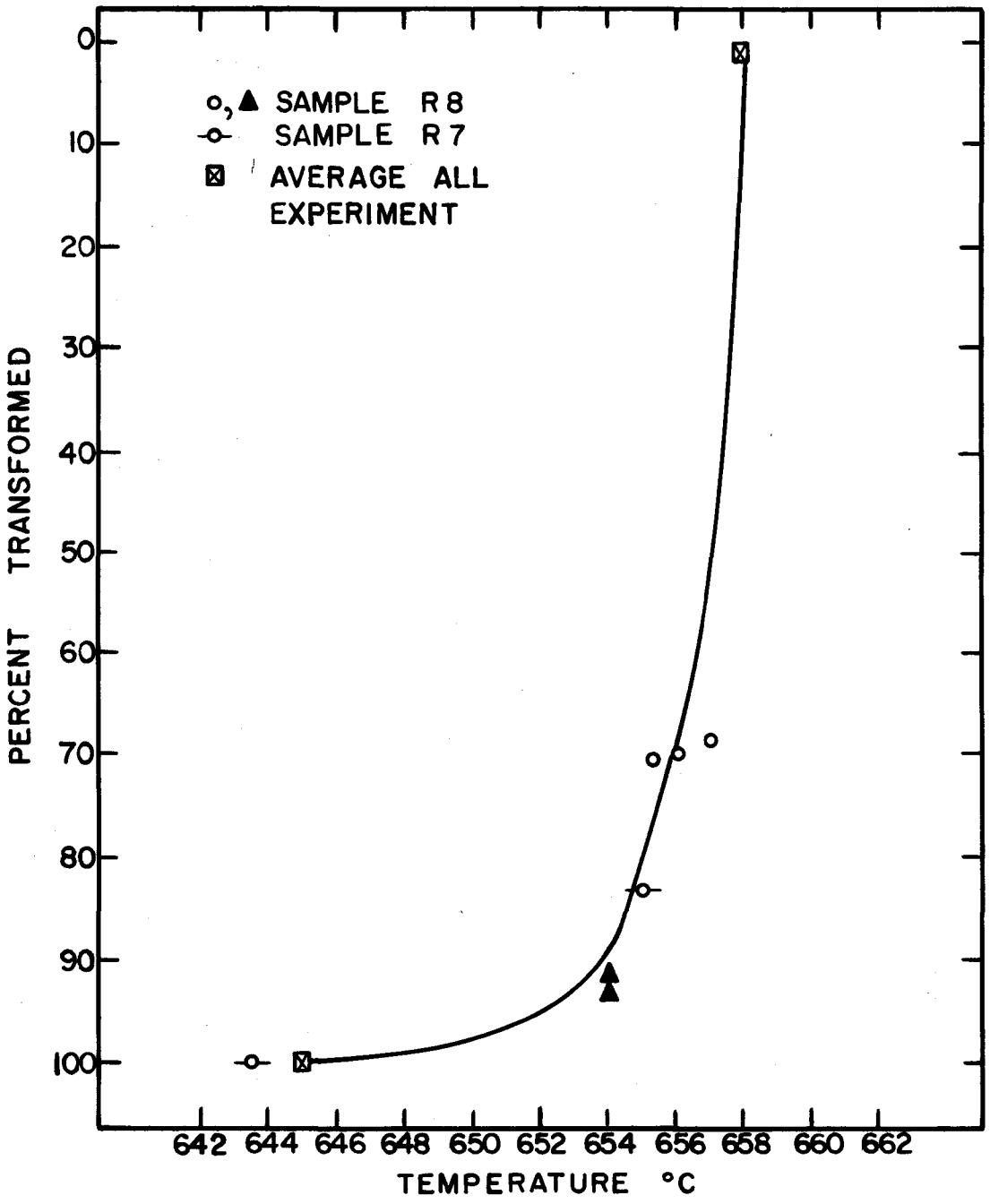


Figure 15. Percent transformed at apparent end of isothermal transformation as a function of temperature for the beta to alpha uranium transformation

used for the martensite transformation in iron-carbon alloys was adopted. The nomenclature is to be interpreted to mean that the β_s temperature on heating, for instance, is the temperature at which beta starts to form, i.e., below which no isothermal transformation of alpha to beta uranium was observed; β_f is the temperature above which isothermal transformation to beta uranium went to 100% completion. On heating the β_s temperature was determined to be 666 $\pm$ 2°C and the β_f temperature was 690 $\pm$ 10°C for the alpha to beta transformation. For the beta to gamma transformation the corresponding temperatures were γ_s = 776 $\pm$ 3°C and γ_f = 786 $\pm$ 4°C.

On cooling the β_s temperature was found to be 772 $\pm$ 5°C and the β_f temperature 761 $\pm$ 3°C for the gamma to beta transformation. For the beta to alpha transformation the values were α_s = 658 $\pm$ 5°C, and α_f = 645 $\pm$ 5°C.

After the apparent end of isothermal transformation on heating or cooling for both transformations, the resistance change could be caused to reverse by heating or cooling the sample, as the case required. The reversal, however, involved a hysteresis of about 8°C for both transformations.

Analysis of these data give the equilibrium temperatures for the allotropic transformations in uranium to be 662 $\pm$ 3°C for the alpha-beta transformation and 774 $\pm$ 4°C for the beta-gamma transformation.

The critical temperatures determined for the allotropic

transformations in uranium are summarized in Table 2.

The temperatures for the allotropic transformations of uranium reported by six different investigators have been summarized by Duwez (21). The temperatures reviewed for the

Table 2. Critical temperatures for the allotropic transformations in uranium

Alpha-beta Equilibrium temperature: 662 ± 3°C	Beta-gamma Equilibrium temperature: 774 ± 4°C
Cooling	
α_s = 658 ± 5°C	β_s = 772 ± 5°C
α_f = 645 ± 5°C	β_f = 761 ± 3°C
Heating	
β_s = 666 ± 2°C	γ_s = 776 ± 3°C
β_f = 690 ± 10°C	γ_f = 786 ± 3°C

alpha-beta transformation ranged from 645 to 675°C; the average of these values is 662°C. The temperatures for the beta-gamma transformation ranged from 764 to 780°C; their average is 772°C. These average values are in agreement with those reported by Moore and Kelley (38) and agree within the experimental limits with the values for the equilibrium temperatures determined in this investigation.

The observations reported in this section can be summarized simply. The allotropic transformations in high

purity uranium proceed isothermally, but the limiting percent transformed isothermally is a function of temperature over a definite temperature range. This was also the case reported by White (22) for the low-temperature beta to alpha transformation of low-chromium uranium-chromium alloys.

The percent transformed is observed to be a function of temperature in typical martensitic transformations also. The distinguishing feature in the case of the uranium transformations is the slower approach to the limiting amount transformed at any given temperature. The results of the experimental examination of this distinguishing feature are reported in the following section.

Kinetic Features of the Transformations

From the analysis of isothermal resistance-time curves for 0.025 inch diameter uranium wire samples, certain characteristics of kinetics of the allotropic transformations have been deduced.

The data from the time-resistance recorder charts were tabularized and converted to percent transformed versus time data. For this purpose the relationship

$$T = \frac{\Delta R_t \times 100}{\Delta R_T} \qquad 9.$$

was used where ΔR_t was the measured change in resistance from the beginning of transformation to time t, ΔR_T was the total change in resistance accompanying the complete trans-

formation including the changes on subsequent step-wise and slow heating to completion, and T was taken as the volume percent of product formed isothermally in time t. Allowances were made for transformation on heating or cooling before the temperature was leveled off to a constant value.

For conciseness these data were graphically summarized on percent transformed versus log time plots. These plots were of a general sigmoid shape. Representative plots of this type for heating and cooling are shown in Figures 16 and 17. The step-wise change in isothermal resistance as a function of time is reflected by the experimental points on these curves and was particularly pronounced for the beta to alpha transformation. It should be noted that the isothermal resistance-change steps were as much as ten times what could be accounted for due to the "dead spot" sensitivity of the recording potentiometer.

A straight line plot of the percent transformed versus time data was then sought. Such data might be expected to give straight line plots if the proper choice of ordinate and abscissa is made. The choice would be quite clear if the function were known which correctly describes the kinetics involved in the reaction. Straight line plots for various typical solid state transformations are known but, excluding the case of classical growth of incoherent nuclei, are largely empirical (22). The empirical plots have the advantage of clarity in summarizing experimental data. Further-

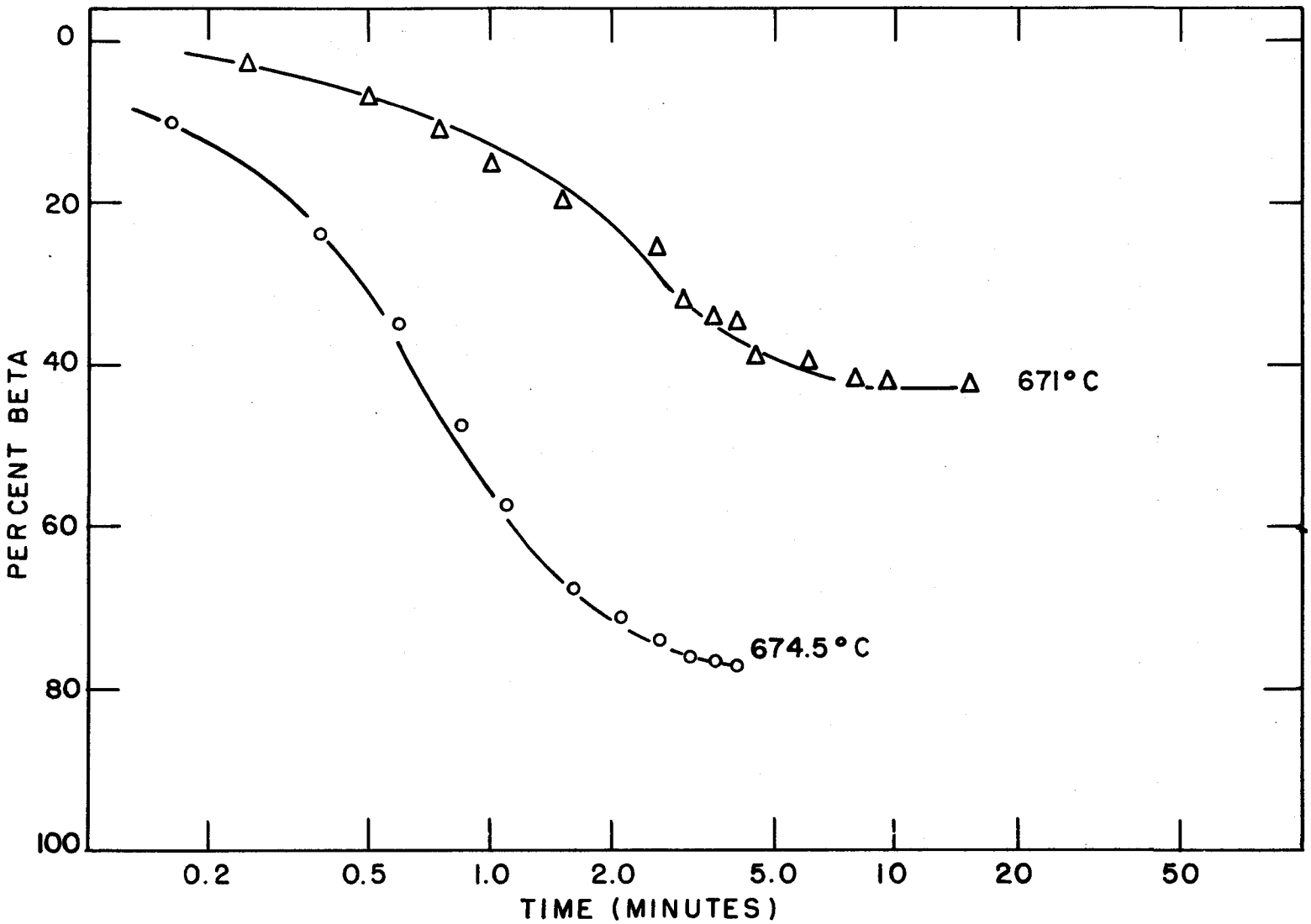


Figure 16. Percent transformed versus log time for the isothermal transformation of alpha to beta uranium at the temperatures indicated

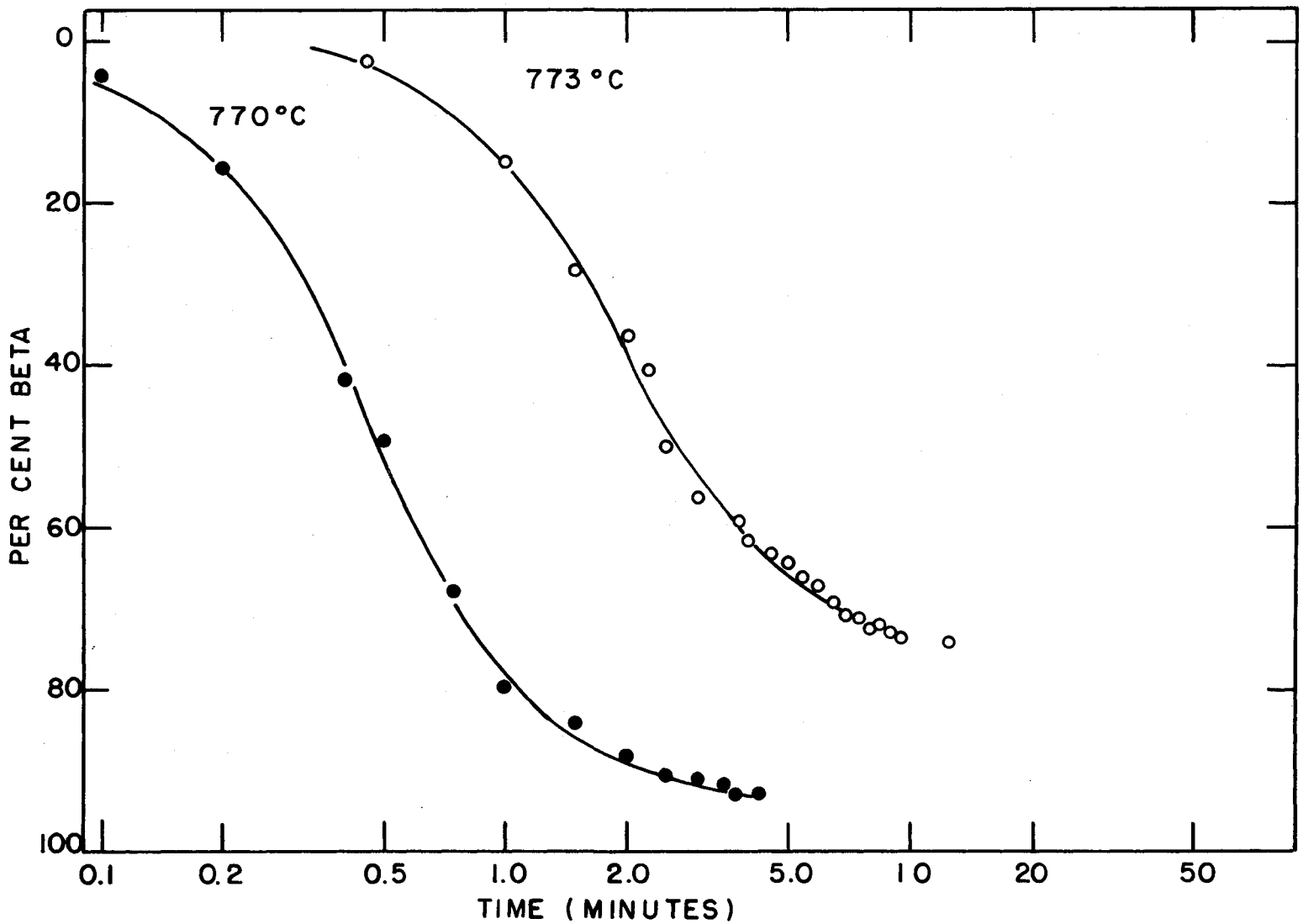


Figure 17. Percent transformed versus log time for the isothermal transformation of gamma to beta uranium at the temperatures indicated

more, these plots tend to classify transformations having certain features in common even if these features are not yet expressible analytically.

It seems apparent that any function describing the kinetics of the isothermal transformations in uranium as represented by the data presented would be rather complicated in order to account for the step-wise changes in isothermal resistance, i.e., the bursts of transformation activity. Of the plots attempted the empirical plot shown in Figures 18, 19, 20, and 21 most concisely summarizes the data. This type of plot was developed by Austin and Rickett (39) for representation of kinetic data for the bainite transformation in iron-carbon alloys and was used for the same purpose by White (22) for the low-temperature beta to alpha data for uranium-chromium alloys. The ordinate of these plots is on a probability scale; the abscissa is log time. As can be seen from these plots the data for the initial part of the transformation are fairly well represented by a straight line. The departure from this line generally indicates a marked reduction in rate of transformation culminating in the apparent end of transformation.

If the data were analyzed for the rate of transformation as a function of time, the burst-like activity was more dramatically emphasized. A plot of this type is shown in Figure 22. The ordinate for each point was obtained by dividing the percent transformed during the time interval

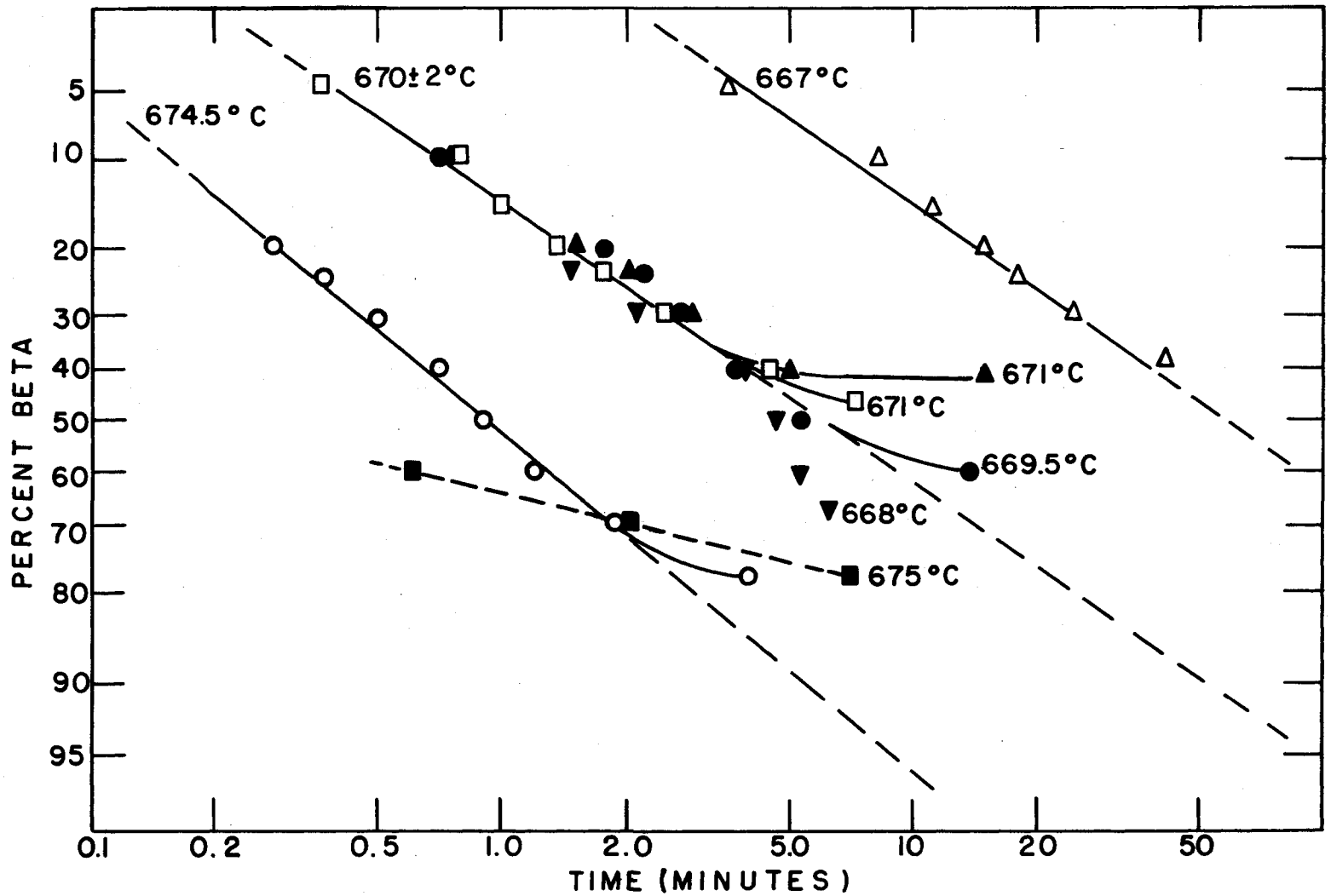


Figure 18. Kinetic data for isothermal transformation of alpha to beta uranium at the temperatures indicated, percent beta formed on a probability scale versus time on a log scale

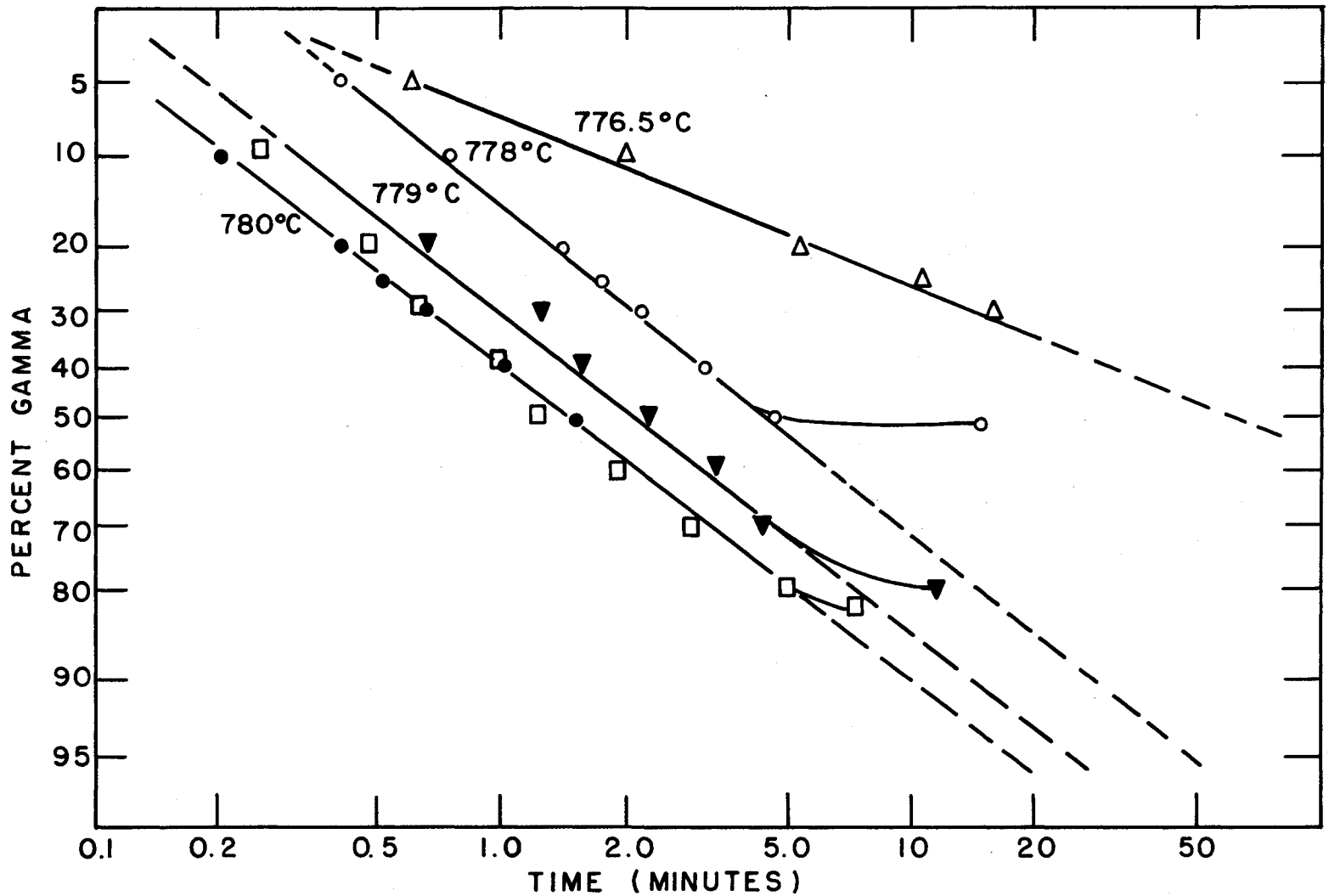


Figure 19. Kinetic data for isothermal transformation of beta to gamma uranium at the temperatures indicated, percent gamma formed on a probability scale versus time on a log scale

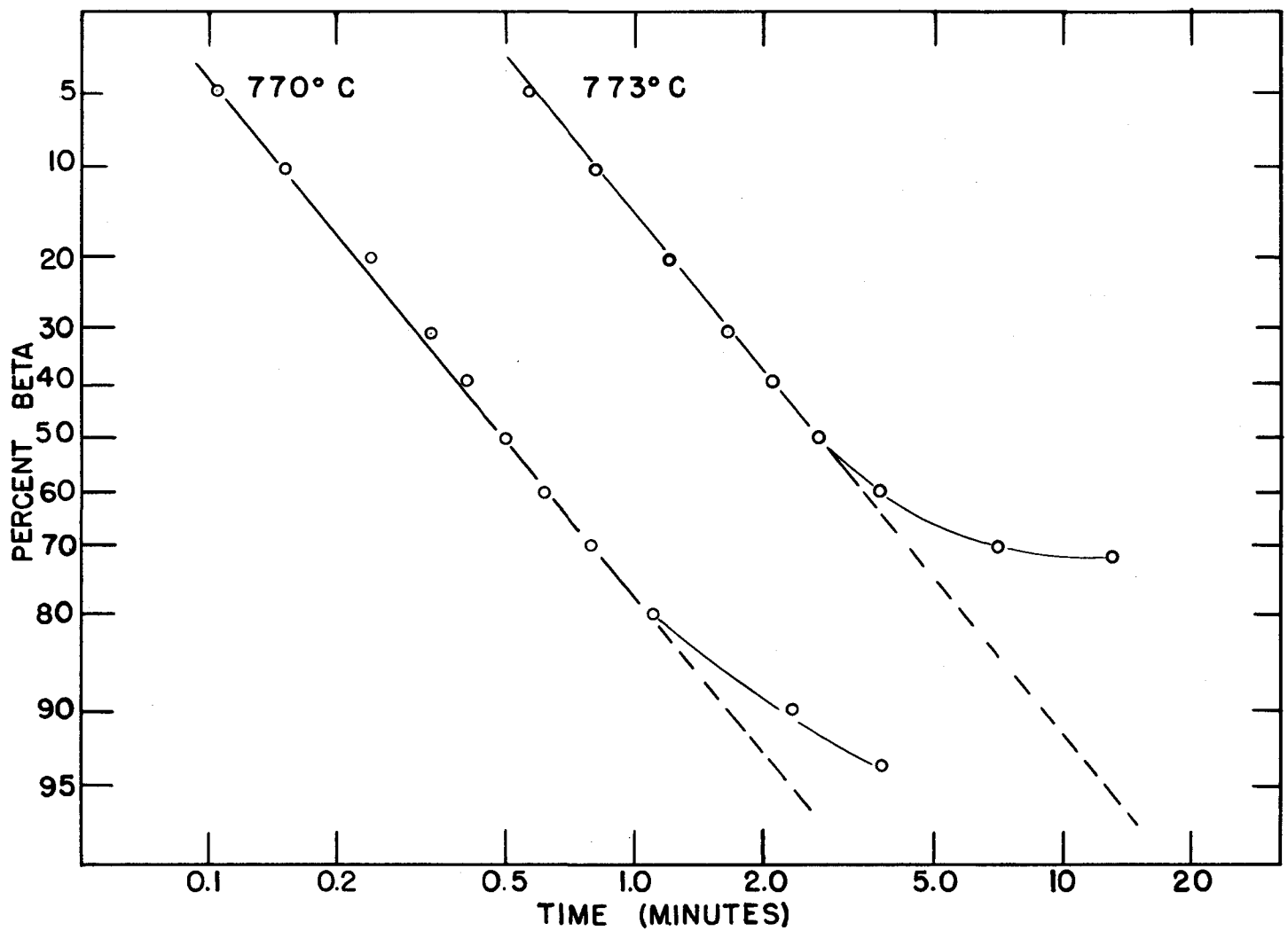


Figure 20. Kinetic data for isothermal transformation of gamma to beta uranium at the temperatures indicated, percent beta formed on a probability scale versus time on a log scale

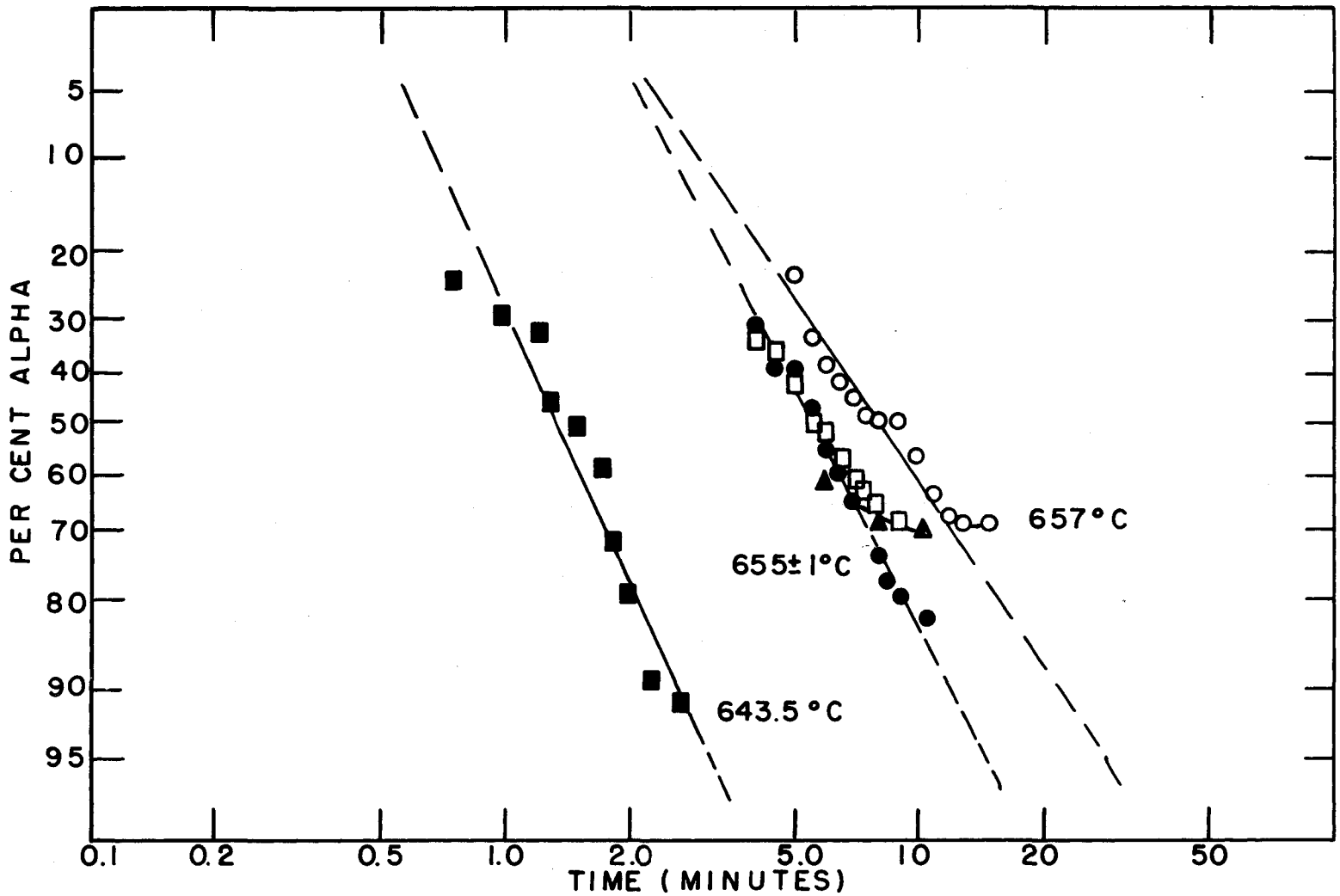


Figure 21. Kinetic data for isothermal transformation of beta to alpha uranium at the temperatures indicated, percent alpha formed on a probability scale versus time on a log scale

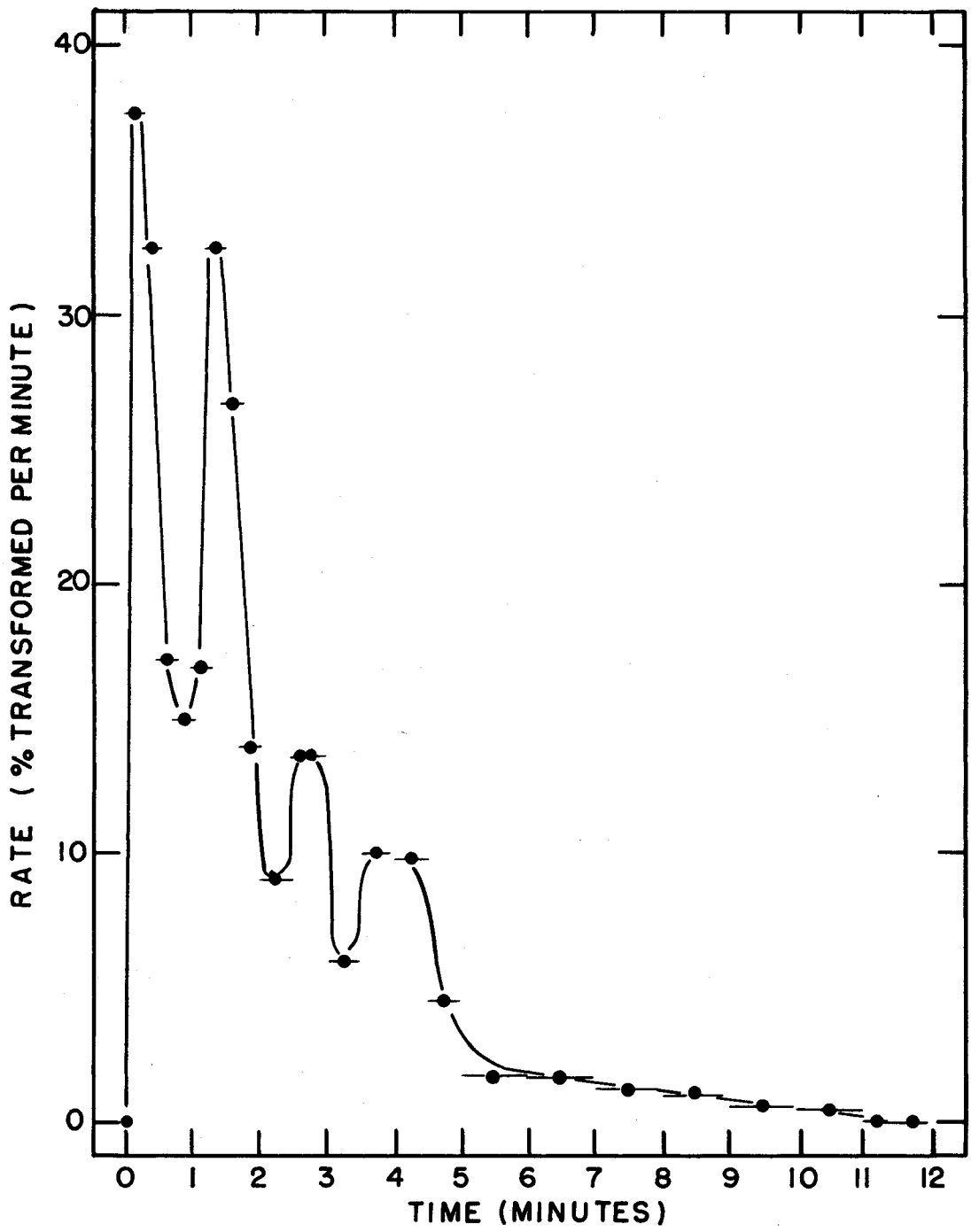


Figure 22. Rate of isothermal transformation as a function of time for the beta to gamma uranium transformation at 779°C

indicated by the horizontal bars on each point of the plot by that time interval. The abscissa of the plot is the time elapsed during isothermal transformation. The limits of experimental error could possibly permit apparent variations in rate of as much as 4%, but effects larger than this must be considered real. The final decrease in rate to the low level at which the transformation apparently completes itself corresponds to the point at which the data begin to deviate from the straight line probability versus log time plots. The maxima for curves of the type shown in Figure 22 increase rapidly when the degree of supercooling or superheating is increased. The increase being a factor of 10 for a 3°C increase in superheat for the beta to gamma transformation. These plots also suggest that if sufficient time were allowed to elapse isothermal transformation might possibly have been observed to continue very slowly beyond the apparent end of transformation. The experimental apparatus employed, however, was not well suited for verification of this point.

In summarizing the kinetic features of the transformation in uranium it can be said that the overall isothermal reactions are relatively slow. They involve initial bursts of transformation activity followed by very slow approach to an apparent end of transformation. The percent-transformed-versus-isothermal-time data for the initial activity can be fairly well represented by straight line plots of a type previously reported (39, 22) for transformations involving the slow

growth of coherent nuclei. The maximum initial rate of transformation was observed to increase rapidly with increasing degree of supercooling or superheating within the range of temperatures which could be profitably studied. Possible interpretations of these features will be suggested below.

The straight line plots of the kinetic data suggest that the allotropic transformations in uranium involve the slow growth of coherent nuclei. As was pointed out in the introduction, such slow growth is not unreasonable. Some indication of the rate-controlling factor must, however, be sought.

Holden (13) has suggested, in explaining the slow coherent growth of alpha needles in uranium-chromium alloys at room temperature, that the retarding process is the requirement of a build up of the transformation stresses to a critical value before they can be relieved by twinning of the alpha product. At these temperatures he showed that twinning of the alpha is the only highly probable mode of relief of these stresses by deformation. Elastic stress below this critical value would tend to oppose the transformation by Le Chatelier's Principle. Thus, the rate-controlling factor was suggested to be the availability of modes of deformation for relieving the transformation stresses.

At the temperatures investigated in the experiments reported here it is reasonable to expect that relief of the transformation stresses will be largely by deformation of the softer alpha and gamma phases. The modes of deformation in

beta uranium at high temperatures have not been reported, but the beta phase is known to be much harder than either of the other phases at the transformation temperatures (40). Cahn (8) has reported that alpha uranium may deform by slip, cross-slip, kinking, and poligonization above 400°C. Gamma uranium is known to be extremely plastic at the transformation temperature as is to be expected from its crystal structure. The relative orientation of the phases involved in coherent transformation may restrict the number of possible deformation modes actually available for stress relief. Thus, the limited availability of modes of deformation for relief of transformation stresses in pure uranium is very probably one of the rate-controlling factors in the slow growth of coherent nuclei. It should also be noted that at the small degrees of superheating and supercooling examined in this investigation, the negative chemical free energy or maximum driving force for the reaction is certainly small.

The bursts of transformation activity must be due to one of two events. Either a large number of the nuclei present at any given time suddenly grow at an accelerated rate or more nuclei are suddenly formed and grow rapidly.

If the proposals by Knapp and Dehlinger (14) about the kinetics of coherent transformations are consulted, an uneven rate of isothermal growth of coherent nuclei already present is not unreasonable. Referring to Equation 1, this uneven growth rate can be related to a change in the balance between

the distortion energy term e_v and the fixed chemical free energy term f_c. Any sudden relief of transformation stresses by deformation would decrease the positive distortion energy term and increase the effective driving force for further growth.

These same proposals also suggest a possible mechanism for the sudden formation and growth of more nuclei. Since it is proposed that "preformed nuclei" can be activated by external stresses on the metal, it is possible that internal stresses, generated in the metal by the growth of the nuclei already present, are effective in activating more "preformed nuclei" for growth.

The very slow rate of transformation observed in the final stages of isothermal transformation may reflect the very slow growth of coherent nuclei whose more rapid growth has been stopped due to strain energy considerations. This slow growth may be the result of stress relief by a process similar to creep.

Lattice Parameters of Uranium as a Function of Temperature

The lattice parameters of uranium have been determined over the temperature range from room temperature to the melting point from high-temperature x-ray diffractometer data. The thermal expansion of the metal at any temperature along the major crystallographic axes can be determined from these data

as can the volume changes accompanying the transformations.

Alpha uranium lattice parameters

The experimental values determined for the lattice parameters a, b, and c of the orthorhombic alpha phase between 20°C and 600°C are given in Table 3. The curves for lattice parameters as a function of temperature drawn from these data are shown in Figures 23, 24, and 25. The values for the

Table 3. Experimental values for the lattice constants of alpha uranium

Sample number	Temperature °C	Lattice constants (A) a	b	c
1-3	20	2.852_6	5.868_2	4.948_9
3-2	20	2.853_7	5.861_9	4.956_5
BR	27	2.854_3	5.864_1	4.957_5
3-2	101	2.857_8	5.863_6	4.961_6
1-3	105	2.858_2	5.866_0	4.957_8
1-3	200	2.866_2	5.864_9	4.970_5
3-2	204	2.865_7	5.863_4	4.974_1
D	212	2.866_3	5.864_6	4.975_1
1-3	304	2.875_1	5.863_6	4.984_4
3-2	306	2.875_6	5.862_0	4.988_1
1-3	400	2.884_9	5.859_4	4.998_5
3-2	400	2.884_5	5.860_2	4.999_6
1-2	403	2.885_9	5.857_5	5.003_3
1-3	505	2.897_1	5.851_6	5.020_3
3-2	602	2.911_3	5.840_2	5.039_4
1-2	603	2.910_6	5.840_6	5.040_7
1-3	603	2.909_8	5.839_3	5.039_7

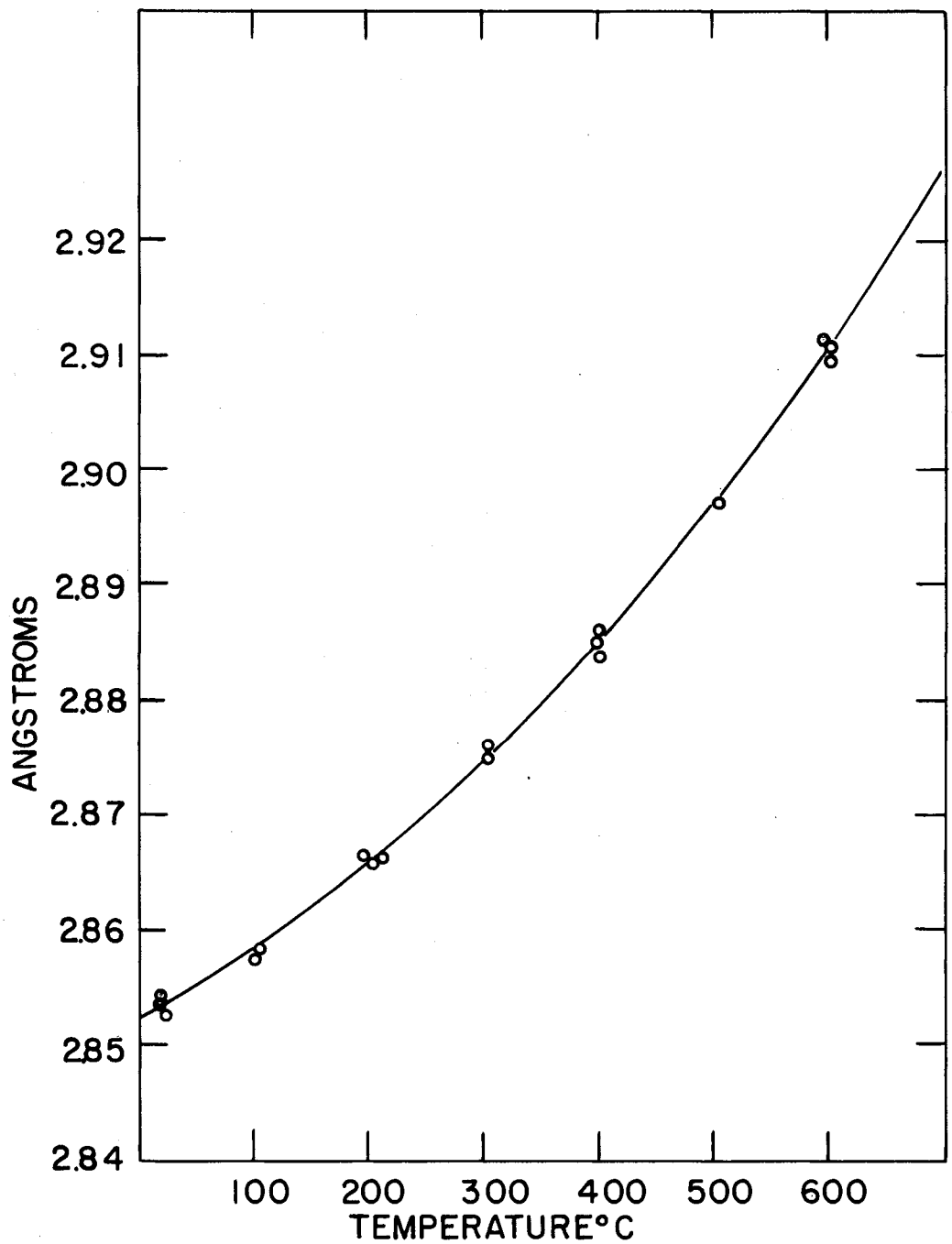


Figure 23. Temperature dependence of the lattice parameter a for orthorhombic (alpha) uranium

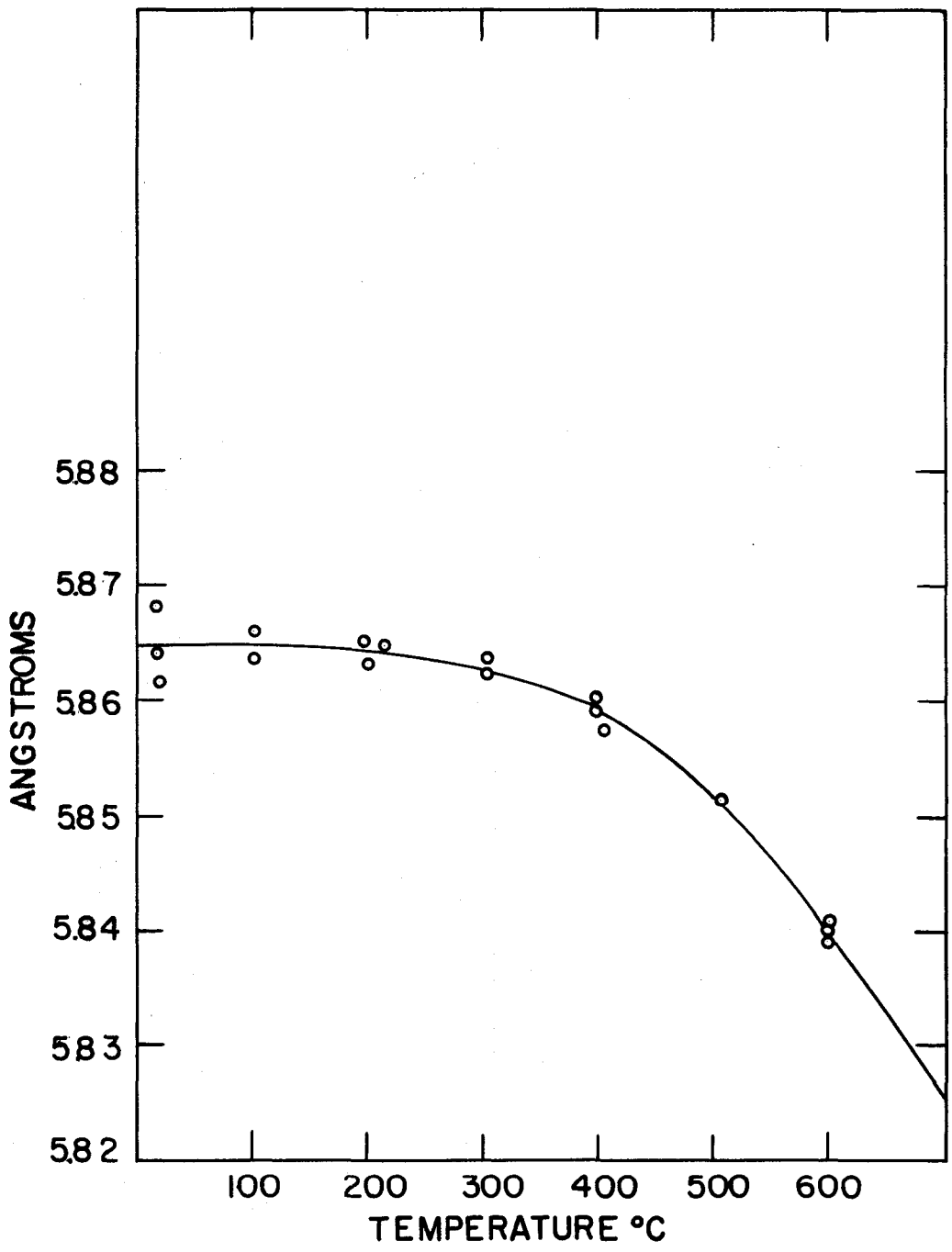


Figure 24. Temperature dependence of the lattice parameter b for orthorhombic (alpha) uranium

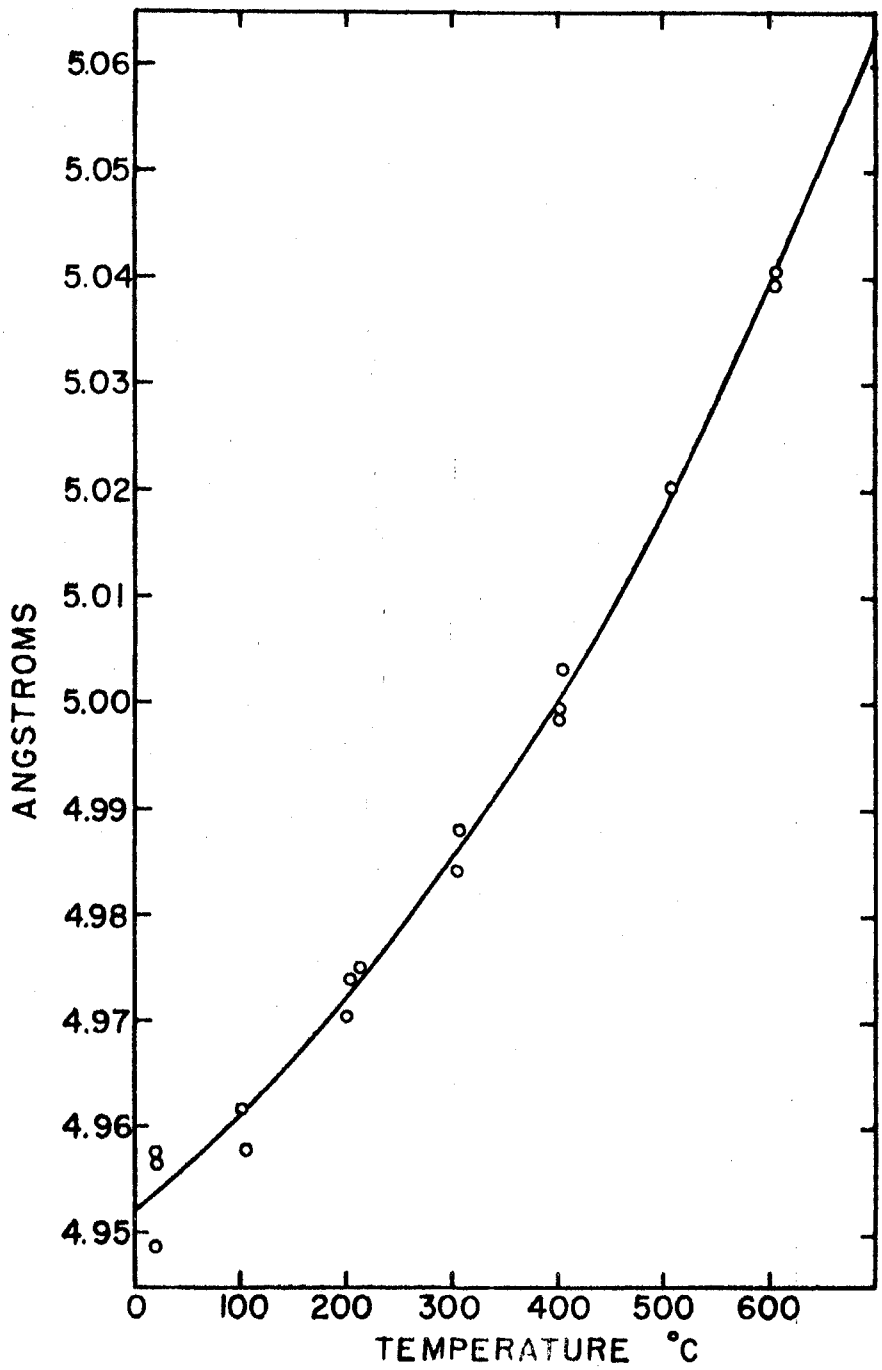


Figure 25. Temperature dependence of the lattice parameter c for orthorhombic (alpha) uranium

constants at 100°C intervals, at room temperature, and at the alpha-beta transformation temperature are given in Table 4 along with calculated volume per unit cell, volume per atom, volume per gram-atom, and density.

Beta uranium lattice parameters

The slopes of the curves describing the lattice parameters of beta uranium as a function of temperature have been determined. These slopes along with the average of three sets of precision lattice parameters (obtained by the modified Cohen extrapolation of diffractometer data) has permitted the construction of curves for the lattice parameters *a* and *c* as a function of temperature.

The experimental values for the lattice parameters at three temperatures and their average are given in Table 5. While the precision of these measurements is surely 0.1% or less, it is to be noted that over the very small temperature range of stability of the beta phase the total change in the parameters is of this same order of magnitude (0.25% for *a* and 0.06% for *c* as will be evident from the final data). This situation makes the proper choice of slope for the best curve through such data alone highly indeterminate. A determination of the slope was, therefore, made independently as described below.

The determination of these slopes was made by calculation from the observed shift in six x-ray diffraction peaks

Table 4. Final x-ray results for alpha uranium

Temperature °C	Lattice constants			Volume		g-atom (cc)	Density (g/cc)
	a	b	c	Unit cell (10^{-24}cc)	Atom (10^{-24}cc)		
0	2.852_3	5.864_9	4.952_2	82.84_3	20.71_1	12.47_3	19.08_6
25	2.853_5	5.864_8	4.954_3	82.91_1	20.72_8	12.48_4	19.07_0
100	2.858_3	5.864_7	4.961_2	83.16_5	20.79_1	12.52_2	19.01_2
200	2.866_0	5.864_1	4.972_2	83.56_5	20.89_1	12.58_2	18.92_1
300	2.874_7	5.862_7	4.985_1	84.01_6	21.00_4	12.65_0	18.82_0
400	2.885_2	5.859_2	5.000_5	84.53_3	21.13_3	12.72_8	18.70_4
500	2.896_9	5.851_6	5.018_7	85.07_5	21.26_9	12.80_9	18.58_6
600	2.910_7	5.839_9	5.040_2	85.67_4	21.41_9	12.90_0	18.45_5
662	2.920_4	5.831_0	5.054_7	86.07_6	21.51_9	12.66_0	18.36_9

Table 5. Experimental lattice constants of beta uranium

Temperature °C	Lattice constants (A) a	c
681	10.758_5	5.653_2
736	10.760_4	5.651_5
765	10.765_1	5.657_0

Average assuming linear change in constants with temperature:

$a = 10.751$
$c = 5.654$ at 727°C

as the temperature was changed in 15°C to 25°C intervals through the beta region. UO_2 and UC reflections were used in correcting the positions of the metal peaks for camera errors. From the corrected reflection angle 2θ for each reflection, the corresponding interplanar spacing d was calculated. These d values were plotted against temperature T. All six of these curves were straight lines showing no evidence of discontinuity or inversion. The six metal peaks were indexed employing the Bunn Chart. These indices were checked using the only available literature value for the constants (41) and the average value for the constants at 727°C reported in Table 5.

It can be shown from the Bragg equation that at a given temperature the axial ratio c/a can be calculated, given the

indices hkl and the interplanar spacing for two independent reflections, i.e., reflections for which $d_1^2 (h_1^2 + k_1^2)$ is not equal to $(h_2^2 + k_2^2)\, d_2^2$ and $d_1^2 \cdot l_1^2$ is not equal to $l_2^2 \cdot d_2^2$. The expression derived is

$$c/a = \left[\frac{d_1^2 l_1^2 - d_2^2 l_2^2}{d_2^2 (h_2^2 + k_2^2) - d_1^2 (h_1^2 + k_1^2)} \right]^{1/2} \qquad 10.$$

In this case the reflections observed were indexed to be the (320), (511), (202), (540), (522), and (621). The above calculation was made for all permissible pairs of reflections, taking the d values from the experimental d versus T plots, at 25°C intervals in the beta region. Average values of c/a in each interval were calculated. Then from the expression

$$a = d_{hkl} \left[h^2 + k^2 + \left(\frac{a^2}{c^2}\right) l^2 \right]^{1/2} \qquad 11.$$

a was calculated at 25°C intervals from each of the six d values and the average c/a value at this temperature. These data were plotted and the slope $\frac{d(a)}{dT}$ for each was measured. These values are shown in Table 6.

The slope $\frac{d(a)}{dT}$ can also be calculated from the measured slope of the d versus T plots. Taking the derivative of both sides of Equation 11 with respect to temperature one gets

$$\frac{d(a)}{dT} = \frac{d(d)}{dT} \left[h^2 + k^2 + (a^2/c^2)\, l^2 \right]^{1/2} + \frac{a l^2}{2} \cdot \frac{d(a^2/c^2)}{dT} \left[h^2 + k^2 + \left(\frac{a^2}{c^2}\right) l^2 \right]^{-1} \qquad 12.$$

Table 6. Calculated change in lattice parameters with temperature for beta uranium in A per °C

hkl	$\frac{d(a)}{dT}$ Calculated from Equations 10 and 11	$\frac{d(a)}{dT}$ Calculated from Equation 12
522	26.3×10^{-5}	22.282×10^{-5}
540	21.8×10^{-5}	21.866×10^{-5}
320	18.8×10^{-5}	19.7498×10^{-5}
621	20.1×10^{-5}	20.088×10^{-5}
202	31.3×10^{-5}	31.285×10^{-5}
511	27.0×10^{-5}	37.782×10^{-5}

hkl	$\frac{d(c)}{dT}$ Calculated from Equations 10 and 13	$\frac{d(c)}{dT}$ Calculated from Equation 14
522	1.4×10^{-5}	3.046×10^{-5}
540	1.2×10^{-5}	3.949×10^{-5}
320	0.4×10^{-5}	2.330×10^{-5}
621	0.2×10^{-5}	2.812×10^{-5}
202	6.3×10^{-5}	6.694×10^{-5}
511	4.0×10^{-5}	8.316×10^{-5}

Here $\frac{d(d)}{dT}$ is measured, $\underline{a}$ is the average value from the Cohen extrapolations, and $\frac{d(a^2/c^2)}{dT}$ and a^2/c^2 are calculated from the c/a data obtained above. Such calculations were made for each reflection and these results are also shown in Table 6.

The average slope from the 12 values in Table 6 is

$$\frac{d(a)}{dT} = 24.8 \times 10^{-5} \text{ A per } ^{\circ}C$$

The average value of $\underline{a}$ from the Cohen extrapolations is

$$a = 10.761 \pm .005 \text{ A at } 727 \pm 3^{\circ}C$$

Since the $\underline{d}$ versus $\underline{T}$ plots were linear and the calculated $\underline{a}$ versus $\underline{T}$ plots were linear, these two values determine the plot of $\underline{a}$ versus temperature for the beta uranium. The coefficient of thermal expansion α in the 100 and 010 directions can be calculated using an extrapolated $0^{\circ}C$ value of $\underline{a} = 10.581 \pm .005$ A to be

$$\alpha \langle 100 \rangle = \frac{a_{775^{\circ}C} - a_{675^{\circ}C}}{a_{0^{\circ}C}\ (100^{\circ}C)} = 23.4 \pm 1.5 \times 10^{-6} \text{ per } ^{\circ}C$$

Exactly similar calculations with regard to the 001 direction in beta uranium employing the equations

$$c = d_{hkl} \left[(c^2/a^2)\ (h^2 + k^2) + l^2 \right]^{1/2} \qquad 13.$$

and

$$\frac{d(c)}{dT} = \frac{d(d)}{dT} \left[(c^2/a^2)\ (h^2 + k^2) + l^2 \right]^{1/2} + \frac{c(h^2 + k^2)}{2} \cdot \frac{d(c^2/a^2)}{dT} \left[(c^2/a^2)\ (h^2 + k^2) + l^2 \right]^{-1} \qquad 14.$$

give

$$\frac{d(c)}{dT} = 3.4 \times 10^{-5} \text{ Å per } ^{\circ}C$$

From the Cohen extrapolation

$$c = 5.654 \pm .005 \text{ A at } 727 \pm 3^{\circ}C$$

and by extrapolation

$$c = 5.409 \pm .005 \text{ A at } 0^{\circ}C$$

giving

$$\alpha \langle 001 \rangle = \frac{c_{775^\circ C} - c_{675^\circ C}}{c_{0^\circ C}\ (100^\circ C)} = 6.0 \pm 2 \times 10^{-6} \text{ per } ^\circ C$$

The data are summarized in Table 6 and in Figure 26. The final results for the lattice parameters of beta uranium and the calculated density and volume values at 25°C intervals from 650°C to 775°C are given in Table 7. The plot of these calculated values is a straight line in all cases.

Table 7. Final x-ray results for beta uranium

Temperature °C	Lattice constants a	Lattice constants c	Volume Unit cell (10^{-24}cc)	Volume Atom (10^{-24}cc)	g-atom (cc)	Density (g/cc)
662	10.744_4	5.651_5	652.4_2	21.74_7	13.09_8	18.17_6
675	10.748_0	5.651_8	653.2_1	21.77_6	13.11_5	18.15_4
700	10.754_0	5.652_5	654.0_3	21.80_1	13.13_0	18.13_2
725	10.760_4	5.653_5	654.8_1	21.82_7	13.14_6	18.11_1
750	10.761_5	5.654_3	655.4_2	21.84_7	13.15_8	18.09_3
772	10.771_9	5.655_0	656.1_7	21.87_2	13.17_3	18.07_3

Gamma uranium lattice parameters

Contamination of the metal surface with UO_2 and UC and coarsening of the grain size of samples above 800°C during the time necessary to record diffraction peaks proved troublesome. Large grain size and the resulting non-random orienta-

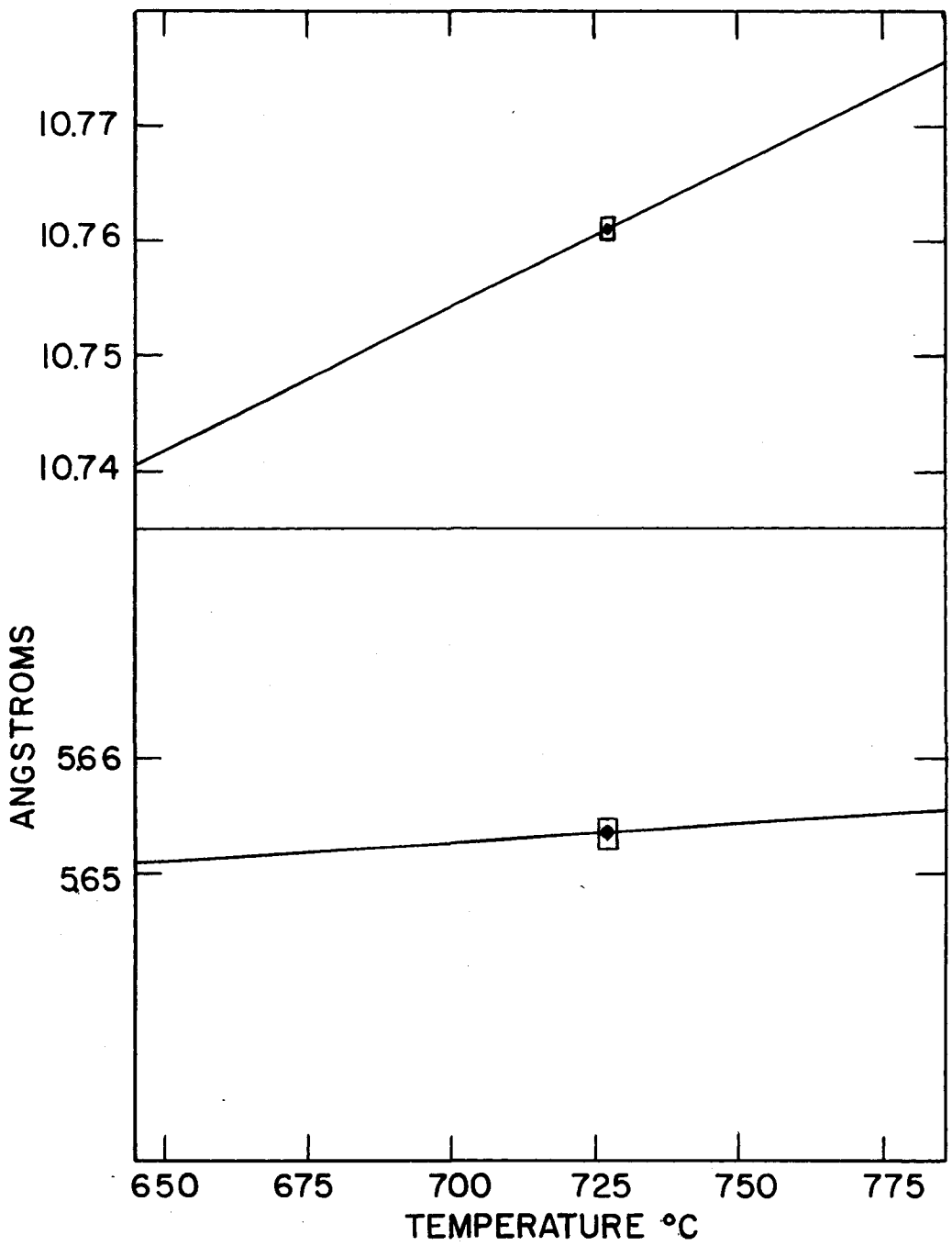


Figure 26. Temperature dependence of the lattice parameters a (top) and c (bottom) for tetragonal (beta) uranium

tion of the grains reduces the number of reflections picked up by the Geiger-counter diffractometer. However, two pure uranium samples each gave two well defined metal reflections showing α_1 and α_2 resolution at 800°C, 900°C, and 1005°C. A larger number of gamma peaks were obtained by employing uranium-zirconium alloy samples. Measurements were made on alloys containing 0.5, 2.5, 5.0, 10.0 and 20.0 weight percent zirconium. Four to six metal reflections were recorded with each of these alloys at 800°C, 900°C, 1005°C, and 1060°C. The constants were refined using the UO_2 and UC reflections as an aid in choosing the proper slope for the Nelson-Riley plots. The values for the refined parameters at each temperature were extrapolated to zero percent zirconium. The extrapolated values for the lattice constant a were in good agreement with those obtained with pure uranium. These data are presented in Table 8, and Figure 27 was drawn from the

Table 8. Experimental lattice constants of gamma uranium

Temperature °C	Lattice constant (A)	
	Ames Biscuit uranium	Extrapolated from U-Zr alloys
800	3.535_4	3.534_0
900	3.542_0	3.540_5
1005	3.549_2	3.550_6
1060	--	3.555_0

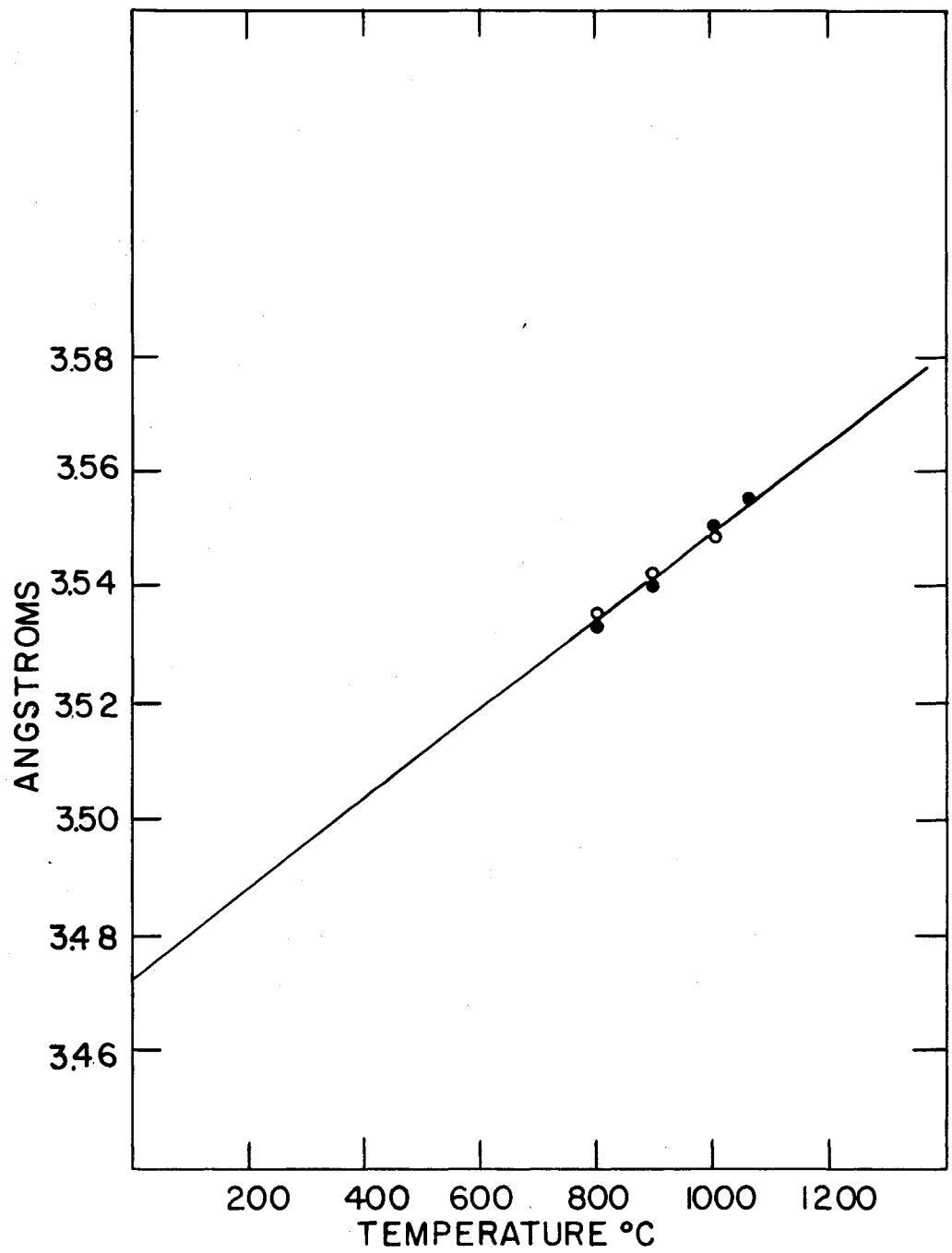


Figure 27. Temperature dependence of the lattice parameter a for body centered cubic (gamma) uranium

experimental data giving an extrapolated room temperature value of 3.472_1 A. The coefficient of thermal expansion from 0°C to 1100°C is calculated to be

$$\alpha_{0°C - 1100°C} = \frac{3.5581 - 3.4721}{3.4721(1100)} = 22.5 \pm 1.3 \times 10^{-6} \text{ per } °C$$

The final values from the plot of the parameter at various temperatures along with the calculated volume per cell, volume per atom, volume per gram-atom, and density are given in Table 9. Calculated densities for all three phases are presented in Figure 28.

Table 9. Final x-ray results for gamma uranium

Temperature °C	Constant a	Volume: Unit cell (10^{-24}cc)	Volume: Atom (10^{-24}cc)	Volume: g-atom (cc)	Density (g/cc)
772	3.532_1	44.06_5	22.03_3	13.27_0	17.94_1
800	3.534_0	44.13_7	22.06_9	13.29_1	17.91_2
850	3.538_0	44.28_7	22.14_4	13.33_6	17.85_0
900	3.542_0	44.43_7	22.21_9	13.35_9	17.79_1
950	3.545_8	44.58_0	22.29_0	13.42_5	17.73_4
1000	3.549_8	44.73_1	22.36_6	13.47_0	17.67_4
1050	3.553_5	44.87_1	22.43_6	13.51_2	17.61_7
1100	3.557_2	45.01_2	22.50_6	13.55_4	17.56_5

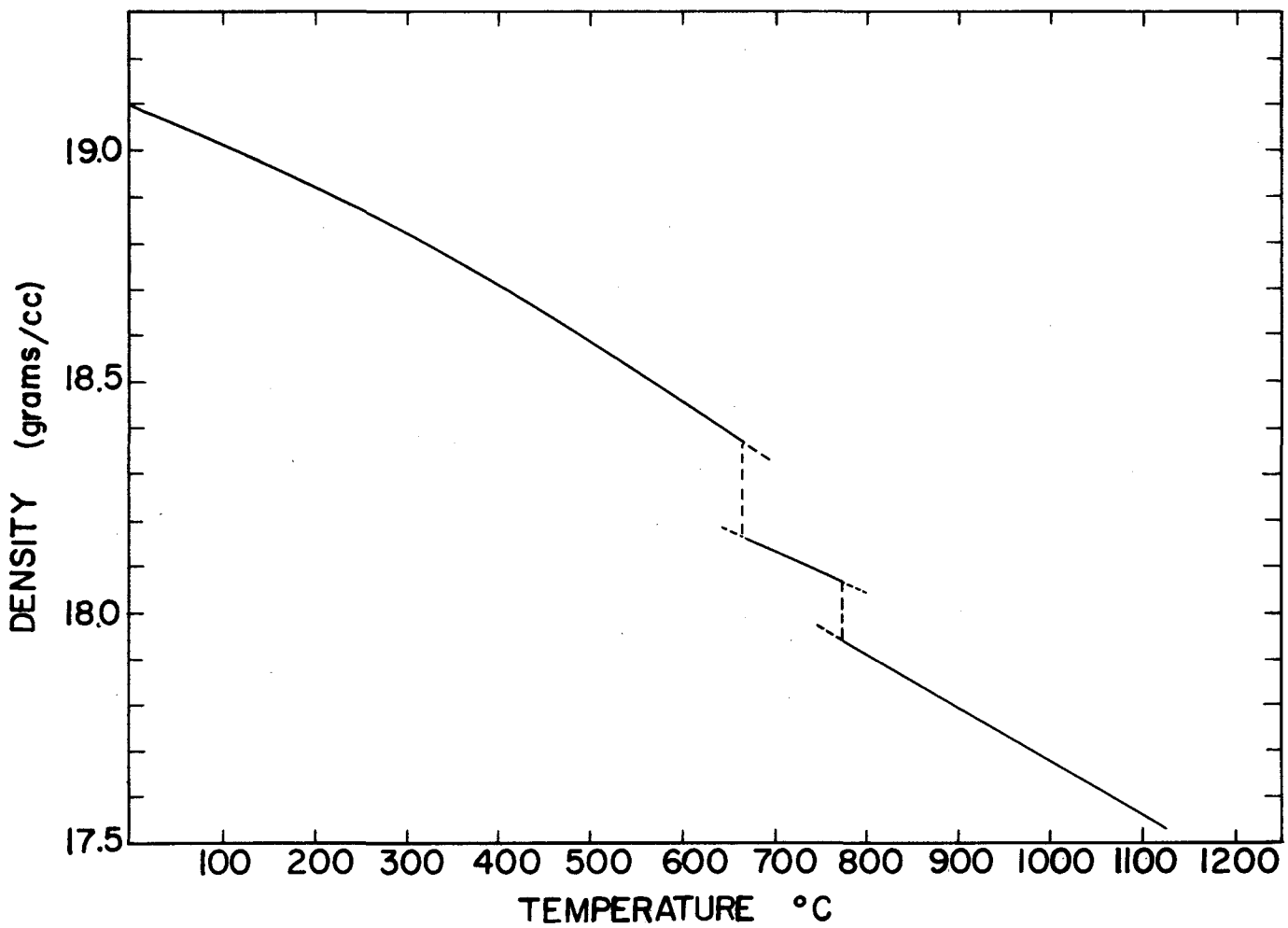


Figure 28. Density of high-purity uranium as a function of temperature calculated from x-ray data

High temperature lattice parameters of UO_2 and UC

It was found desirable to use the lattice parameters of UO_2 and UC as internal standards and as an aid in indexing the tetragonal uranium patterns taken at temperature. The lattice parameters of uranium dioxide and uranium monocarbide in the beta temperature range and the thermal expansion of these materials in the form of a surface film on massive uranium from 0°C to 800°C has been determined.

The lattice parameters of these compounds, present as a surface film on massive uranium, were determined from x-ray diffractometer data taken at temperature in the course of the studies on uranium. The average of six such determinations at 717°C gave

$$a_{UO_2} = 5.496 \pm .005 \text{ A}$$

and

$$a_{UC} = 4.973 \pm .005 \text{ A}$$

The thermal expansion was determined by recording at 25°C intervals the position of the (200) peaks from the UO_2-UC film on a uranium sample. From these data a plot of apparent lattice parameter versus temperature could be drawn for each compound. These plots were both straight lines above about 200°C. Departure from linearity, corresponding to a more rapid decrease in lattice parameters, was observed in the temperature range from 200°C to room temperature. This curved

portion of the plot is interpreted as due to the residual compressive stresses in the film which result from the relatively larger thermal contraction of the uranium on cooling. (The magnitude of the compressive strain can be calculated from the curves to be 0.3 ± .1% at room temperature.) The straight line portions of the plots were extrapolated to 0°C. The coefficient of thermal expansion α between 0°C and 800°C was found to be 7.6 ± 0.7 x 10^{-6} per °C for both uranium dioxide and uranium carbide.

These plots were corrected for camera errors using the accepted value for the lattice parameter of UO_2 at room temperature, a = 5.4682 A (41). These values provided an independent check on the lattice parameters determined directly from beta region data. The values found from the thermal expansion curves at 717°C were

$$a_{UO_2} = 5.497 \pm .003 \text{ A} \quad \text{and} \quad a_{UC} = 4.964 \pm .003 \text{ A}$$

in good agreement with the values reported above.

Evaluation of x-ray results

The final results for the lattice parameters of alpha uranium agree with the powder x-ray values reported by Bridge, Schwartz, and Vaughan (3) within 0.05% for all three parameters at all temperatures with the exception of c above about 500°C. Here the agreement is still quite good, and is within 0.2% at the transformation temperature. These data are also supported by the single crystal dilatometric data of Lehr and Langeron

(43). The decrease in the value of the b parameter with increasing temperature is rather unusual and basic to the understanding of many of the irregular phenomena observed during alpha cycling of uranium (6).

The results from the final curves for beta uranium agree with the data given by Thewlis (41) within the limits of experimental error. His data for low-chromium uranium-chromium alloys are

$$\alpha^{\langle 100 \rangle}_{675^\circ C - 775^\circ C} = 23 \pm 1.4 \times 10^{-6} \text{ per } ^\circ C$$

and

$$\alpha^{\langle 001 \rangle}_{675^\circ C - 775^\circ C} = 4.6 \pm 1.6 \times 10^{-6} \text{ per } ^\circ C$$

He also reports a = 10.759 ± .001 A; c = 5.656 ± .001 A at 720 ± 10°C in excellent agreement with the results of this investigation. The data give no evidence for any discontinuities or change in slope in the curves for lattice parameter versus temperatures in the region of beta stability.

Considering the small number of reflections which could be recorded and the extrapolations involved, the precision in the measurement of the gamma parameters at various temperatures is probably not better than 0.2%. The value of the coefficient of thermal expansion, however, agrees nicely with the value of 22.6 x 10^{-6} per °C from dilatometric measurements on polycrystalline material as determined by Lloyd at the Argonne National Laboratory and reported by Foote (6).

The lattice parameter at 720°C and the coefficient of

thermal expansion for UO_2 measured by Thewlis (41) for UO_2 films on powdered uranium do not agree closely with the results presented here for UO_2-UC films on uranium. His values are

$$a_{UO_2} = 5.512 \pm .005 \text{ A at } 720 \pm 10^{\circ}C$$

and

$$\alpha\ 20^{\circ}C - 720^{\circ}C = 11.5 \pm 1.7 \times 10^{-6} \text{ per } {}^{\circ}C$$

The latter value was calculated from his 720°C parameter and the same value for 20°C as accepted in this work. The discrepancy is very probably due to the difference in composition of the films measured.

The reported data give the volume changes at the transformations as $\Delta V_{\alpha/\beta} = 1.12\%$ and $\Delta V_{\beta/\gamma} = 0.70\%$. These volume changes are somewhat smaller than anticipated considering the large macroscopic distortion known to accompany the transformations.

Considerations on the Crystallographic Features of the Transformations

Phenomenological crystallographic theories for transformations involving the nucleation and growth of coherent nuclei have been developed by Lieberman, Wechsler, and Read (25, 26) and by Bowles and MacKenzie (44, 45, 46, 47). These theories permit the calculation of the crystallographic features of such transformations. Habit plane, shear angle, and the crystallographic relationship of product to parent

phase can be calculated. Only the lattice parameters of the phases at the transformation temperatures and a suitable choice of inhomogeneity such as twinning or slip are needed. The results of the calculation are, in most cases, multiple-valued, and not all of the solutions are observed experimentally. The experimental results, however, in all of the cases treated agree very closely to one consistent set of the calculated features. The calculations have been developed both graphically and in terms of matrix algebra.

The principle on which these calculations are based is that the strain energy involved will be minimized if the boundary plane between the parent and product phase is one of zero average distortion. The basic theorem of the Lieberman, Wechsler, and Read treatment (26) states that the necessary and sufficient condition for the existence of a plane of zero net distortion is that one of the principle distortions be unity, i.e., one of the principle transformation strains vanish. From the lattice parameters of the two phases involved, one can determine if this condition can hold without some inhomogeneity such as twinning or slip in the product phase. That is, homogeneous distortion to give a plane of zero average distortion would be possible if transformation of simple corresponding cells of the two phases can be accomplished by a distortion in which one of the principle distortions is unity.

The lattice parameters for the tetragonal and orthorhombic

phases in uranium at the alpha-beta transformation temperature were reported in the previous section to be

$$a = 10.7444 \text{ A}, \quad c = 5.6515 \text{ A}$$

$$a = 2.9204 \text{ A}, \quad b = 5.8310 \text{ A}, \quad c = 5.0547 \text{ A}$$

The configuration, involving the smallest distortion, which allows the homogeneous transformation of a small region of beta uranium to alpha uranium was sought. The corresponding primary cells must quite obviously contain an equal number of atoms. The orthorhombic unit cell contains four atoms and the tetragonal unit cell contains 30 atoms. Therefore, the smallest possible primary cells must both contain 60 atoms. The configuration, shown in Figure 29, of all of those considered gave the smallest strain distortions. It is therefore expected to be favored energetically. The primary tetragonal cell has the parameters

$$a_p = \sqrt{2}\, a_\beta = 15.194 \text{ A}$$

$$c_p = c_\beta = 5.6515 \text{ A}$$

The corresponding primary orthorhombic cell has the parameters

$$a_p = 5\, a_\alpha = 14.602 \text{ A}$$

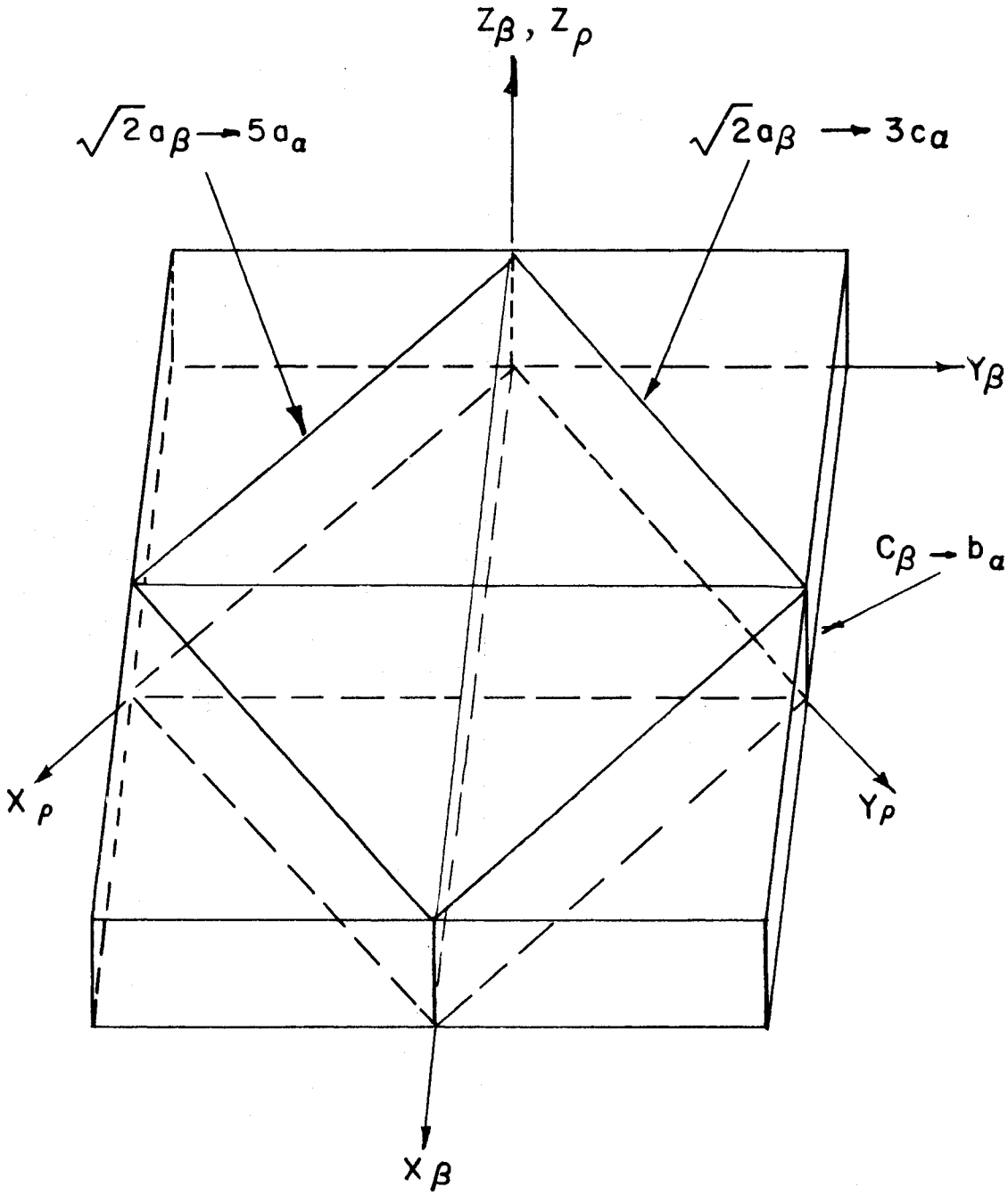
$$b_p = 3\, c_\alpha = 15.164 \text{ A}$$

$$c_p = b_\alpha = 5.8310 \text{ A}$$

The matrix which describes the distortion of this primary tetragonal cell to the corresponding orthorhombic cell dimensions when related to an orthogonal set of axes x_p, y_p, and z_p in the $1\bar{1}0$, 110, and 001 directions, respectively, in the beta unit cell is

Figure 29. Diagrammatic representation of the relation of the corresponding primary cells for homogeneous distortion of beta to alpha uranium

The normal beta lattice directions x_β, y_β, z_β are shown. The primary tetragonal cell (the inner "box" in the figure) is drawn with the principle directions x_p, y_p, z_p indicated. x_p is 45^o from x_β and y_p is 45^o from y_β. The size of primary cell before and after beta to alpha transformation is indicated in terms of the lattice parameters of the two phases.


Z_β, Z_ρ
$\sqrt{2}a_\beta \rightarrow 5a_\alpha$
$\sqrt{2}a_\beta \rightarrow 3c_\alpha$
Y_β
$C_\beta \rightarrow b_\alpha$
X_ρ
Y_ρ
X_β

$$T = \begin{bmatrix} d_1 & 0 & 0 \\ 0 & d_2 & 0 \\ 0 & 0 & d_3 \end{bmatrix} \qquad 15.$$

where

$$d_1 = \frac{b\, a_\alpha}{\sqrt{2}\, a_\beta} = 0.96098, \qquad d_2 = \frac{3\, c_\alpha}{\sqrt{2}\, a_\beta} = 0.99797,$$

$$\text{and } d_3 = \frac{b_\alpha}{c_\beta} = 1.0319$$

Thus, contractions of 3.91% and 0.20% in the $1\bar{1}0$ and 110 directions, and an expansion of 3.18% in the 001 direction, respectively, would be required to homogeneously transform a small region of beta uranium to alpha uranium.

It is interesting to note that the principle distortion d_2 is almost unity. Furthermore, if the alpha lattice parameter $\underline{c}$ extrapolated from the data reported by Bridge, Schwartz, and Vaughan (3) is used, this distortion is calculated to be almost exactly unity. The extrapolated values of $\underline{b}$ and $\underline{a}$ reported by these investigators agree with those used here. Thus the conditions for a plane of zero distortion under homogeneous transformation are nearly met. If it is assumed that d_2 is unity, the unit normal to the interface plane of zero net distortion can be calculated.

If r_β is a unit vector lying in the plane of zero distortion, then by definition it must be unchanged in length by the homogeneous distortion. That is, if r_β lies in the plane of zero distortion and

$$T\, r_\beta = r_\alpha \tag{16.}$$

then

$$|r_\beta| = |r_\alpha| = |T\, r_\beta| \tag{17.}$$

If the components of r_β are along the three principle directions of the primary tetragonal cell x_p, y_p, and z_p, then r_β can be written as the column matrix

$$r_\beta = \begin{bmatrix} x_p \\ y_p \\ z_p \end{bmatrix}$$

and

$$|r_\beta| = (x_p^2 + y_p^2 + z_p^2)^{1/2} \tag{18.}$$

Furthermore,

$$T\, r_\beta = \begin{bmatrix} d_1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & d_3 \end{bmatrix} \begin{bmatrix} x_p \\ y_p \\ z_p \end{bmatrix}$$

$$T\, r_\beta = \begin{bmatrix} d_1 & x_p \\ & y_p \\ d_3 & z_p \end{bmatrix} \tag{19.}$$

and

$$|r_\alpha| = |T\, r_\beta| = (d_1^2 x_p^2 + y_p^2 + d_3^2 z_p^2)^{1/2} \tag{20.}$$

Thus, the condition that r_β lie in the plane of zero distortion implies

$$d_1^2 x_p^2 + y_p^2 + d_3^2 z_p^2 = x_p^2 + y_p^2 + z_p^2 \tag{21.}$$

or

$$(d_1^2 - 1)\, x_p^2 + (d_3^2 - 1)\, z_p^2 = 0$$

Thus

$$\frac{z_p}{x_p} = \left(\frac{1 - d_1^2}{d_3^2 - 1}\right)^{1/2} = \pm K \qquad 22.$$

It follows that a unit vector normal to the plane of zero distortion (which is to be the interface plane or habit plane) is

$$n_p = \frac{1}{(1 + K^2)^{1/2}} \begin{bmatrix} \mp K \\ 0 \\ 1 \end{bmatrix} \qquad 23.$$

Choosing the plus sign for K in Equation 22, numerical substitution gives

$$n_p = \begin{bmatrix} -.7365 \\ 0 \\ .6764 \end{bmatrix}$$

To refer this vector to the normal directions for the beta unit cell axes requires a rotation through 45^0 about the z_p axis so that

$$n_\beta = \begin{bmatrix} .7071 & .7071 & 0 \\ -.7071 & .7071 & 0 \\ 0 & 0 & 1 \end{bmatrix} n_p \qquad 24.$$

giving

$$n_\beta = \begin{bmatrix} .5208 \\ -.5208 \\ .6764 \end{bmatrix}$$

This is close to the normal to the $(2\bar{2}1)$ beta plane. No experimental determination of the habit plane for the beta to alpha transformation in pure uranium has been reported. The unit normals to the reported (13, 23) habit planes for the

room temperatures beta to alpha transformation in low-chromium uranium-chromium alloys are

$$n_\beta(3\bar{2}1) = \begin{bmatrix} .7078 \\ -.4719 \\ .4485 \end{bmatrix} \quad \text{and} \quad n_\beta(4\bar{4}1) = \begin{bmatrix} .6703 \\ -.6703 \\ .3186 \end{bmatrix}$$

So that the plane calculated is $23^\circ\ 21'$ from the $(3\bar{2}1)$ plane and $23^\circ\ 58'$ from the $(4\bar{4}1)$ plane.

This comparison is, however, not necessarily expected to give agreement. The calculation of the habit plane for the uranium-chromium alloys at room temperature will involve different lattice parameters than those used here. The lattice parameters of the two phases depend not only on temperature but on the chromium content. In fact, it may be the case that none of the principle distortions are very near to unity for the alloy transformation. However, Butcher (24) has reported that the orientation of pure uranium alpha grains resulting from the transformation of a beta single crystal of pure uranium could be accounted for on the basis of the orientation relationship determined for the chromium-uranium alloys at room temperature.

The evidence is, then, that for the pure uranium beta to alpha transformation none of the principle distortions are, in fact, exactly equal to unity. That is, the transformation distortion must normally be inhomogeneous.

The calculation of the habit plane and orientation relationships for an inhomogeneous transformation of a tetragonal

to an orthorhombic lattice has not yet been reported. In fact, all of the transformations so far treated by the phenomenological crystallographic theories have involved at least one cubic phase (48).

Lieberman, Wechsler and Read have treated the cubic to orthorhombic transformation in AuCd alloys (26). The primary corresponding cells were chosen in the same orientation suggested here for uranium. The inhomogeneity chosen was twinning in the product phase. However, in order that there be a solution in the treatment as developed the plane in the cubic phase which becomes the twin plane in the product must be a mirror plane. Furthermore, it must not contain any of the principle strain distortions d_1, d_2, d_3. Thus, a simple extension of this treatment to the tetragonal to orthorhombic case is not possible. The symmetry of the tetragonal lattice allows no such choice of twin plane for the suggested configuration for uranium. This configuration, as stated, apparently involves the smallest strain distortions of any considered.

Christian (48) in his review article on the status of the crystallographic theories implies that the uranium transformations can be treated. Certainly the principle of minimization of the strain energy by a habit plane of zero average distortion must apply. The mathematical treatment will be complicated by the lower symmetry of the phases involved.

The approach to the problem is clearly to develop the

calculations for the uranium-chromium alloy transformation. For this case the experimental observations are available. The calculations for the pure uranium transformation will apparently then be a matter of numerical substitution.

The experimental determination of the crystallographic features of the alpha to beta uranium transformation is complicated by two difficulties. The attenuation in intensity of high angle x-ray diffraction reflections with temperature has been observed to be marked. Back reflection Laue orientation patterns taken at the transformation temperature are not very satisfactory. Secondly, the high x-ray absorption coefficient for uranium also interferes with recording transmission or front reflection Laue patterns even from crystals only about a tenth of a millimeter thick.

In determining the beta-gamma crystallographic features the experimental difficulties are expected to be amplified by the increase in temperature involved. The phenomenological crystallographic calculations should, however, be readily extended to this body centered cubic to tetragonal transformation in uranium.

SUMMARY AND CONCLUSIONS

Resistance effects observed accompanying the alpha-beta transformation in high purity uranium indicate a certain degree of reversibility in the orientation of a given grain on thermal cycling through both transformations. The effect on the alpha-phase thermal twinning temperature, on the resistance of newly-formed alpha, and on the transformation temperatures resulting from rapid thermal cycling of uranium through both allotopic transformations is interpreted to indicate progressive lattice hardening.

It has been shown that the allotropic transformations in uranium proceed isothermally, but that the extent of isothermal transformation is a function of temperature over a definite temperature range. The isothermal transformation initially involves bursts of transformation activity, and proceeds in its later stages very slowly to an apparent end of transformation.

The lattice parameters of high purity uranium from room temperature to the melting point have been experimentally determined. The crystallographic features of the alpha-beta transformation have been discussed in terms of the lattice parameters of the two phases and the volume change at the transformation temperature.

From the evidence presented it is concluded that the allotropic transformations in uranium proceed by the nucle-

ation and slow growth of coherent nuclei. The features of the transformations are closely similar to those of typical martensitic reactions, except for the kinetic features. Arguments have been proposed to explain these non-typical kinetic features.

LITERATURE CITED

1. Jacob, C. W. and B. E. Warren, J. Am. Chem. Soc., 59, 2588 (1937).

2. Tucker, C. W. Jr., Trans. Amer. Soc. Metals, 42, 762 (1950).

3. Bridge, J. R., C. M. Schwartz and D. A. Vaughan, J. Metals, 8, 1282 (1956).

4. Tucker, C. W. Jr., P. Senio, J. Thewlis and H. Steeple, Acta Cryst., 9, 472 (1956).

5. Wilson, A. S. and R. E. Rundle, Acta Cryst., 2, 126 (1949).

6. Foote, F. G., in "International Conference on the Peaceful Uses of Atomic Energy, Proceedings", 9, p. 33, United Nations, New York, 1956.

7. Howe, J. P., in "International Conference on the Peaceful Uses of Atomic Energy, Proceedings", 9, p. 179, United Nations, New York, 1956.

8. Cahn, R. W., Acta Met., 1, 49 (1953).

9. Holden, A. N., Acta Cryst., 5, 182 (1952).

10. Friedel, J., J. Phys. Chem. Solids, 1, 175 (1956).

11. Saller, H. A., in "The Reactor Handbook", 3, p. 383, Technical Information Service U. S. Atomic Energy Commission, Washington, D. C., 1955.

12. Reheman, R. F. and A. R. Troiano, Metals Progress, 70, No. 2, 97 (1956).

13. Holden, A. N., Acta Met., 1, 617 (1953).

14. Knapp, H. and U. Dehlinger, Acta Met., 4, 289 (1956).

15. Bowles, J. S. and C. S. Barrett, in Chalmers, B., Ed., "Progress in Metal Physics", p. 1, Interscience, New York, 1952.

16. Smoluchowski, R., J. E. Mayer and W. A. Weyl, Eds., "Phase Transformations in Solids", Wiley, New York, 1951.

17. Institute of Metals, "The Mechanism of Phase Transformations in Metals", Mono. No. 18, The Institute, London, 1955.

18. Turnbull, D., Metals Technology, 15, Tech. Publ. No. 2365 (1948).

19. Cohen, M., in Smoluchowski, R., J. E. Mayer and W. A. Weyl, Eds., "Phase Transformations in Solids", p. 588, Wiley, New York, 1951.

20. Cahn, R. W., Acta Met., 1, 176 (1953).

21. Duwez, P., J. Appl. Phys., 24, 152 (1953).

22. White, D. W., J. Metals, 7, 1221 (1955).

23. Butcher, B. R. and A. H. Rowe, Nature, 172, 817 (1953).

24. Butcher, B. R., "The Beta to Alpha Phase Change in Pure Uranium, Parts I and II", Atomic Energy Research Establishment, Harwell, Berkshire, England, Report No. A.E.R.E. M/R 1944, 1956.

25. Lieberman, D. S., M. S. Wechsler and T. A. Read, J. Metals, 5, 1503 (1953).

26. Lieberman, D. S., M. S. Wechsler and T. A. Read, J. Appl. Phys., 26, 473 (1955).

27. Chiotti, P., Rev. Sci. Instr., 25, 876 (1954).

28. Chiotti, P., Rev. Sci. Instr., 25, 683 (1954).

29. Nelson, J. B. and D. P. Riley, Proc. Phys. Soc. (London) 57, 160 (1945).

30. Cohen, M. U., Rev. Sci. Instr., 6, 68 (1935).

31. Cohen, M. U., Rev. Sci. Instr., 7, 155 (1936).

32. Wilson, A. J. C., J. Sci. Instr., 27, 321 (1950).

33. Burke, J. E. and A. M. Turkalo, J. Metals, 4, 651 (1952).

34. Bettman, M., G. W. Brown and J. P. Frankel, "On the Dimensional Instability of Uranium and of Clad Plates Subjected to Thermal Cycling", Livermore Research Laboratory, Livermore, California, Report No. MTA - 36, 1953.

35. Glen, J. W. and S. F. Pugh, "Transformations Between Hexagonal and Body Centered Cubic Lattices", Atomic Energy Research Establishment, Harwell, Berkshire, England, Report No. A.E.R.E. M/R 1144, 1953.

36. Fisher, J. C. and D. Turnbull, Acta Met., 1, 310 (1953).

37. Patel, J. R. and M. Cohen, Acta Met., 1, 531 (1953).

38. Moore, G. E. and K. K. Kelley, J. Amer. Chem. Soc., 69, 2105 (1947).

39. Austin, J. B. and R. L. Rickett, Metals Technology, 5, Tech. Publ. No. 964 (1938).

40. Chubb, W., J. Metals, 7, 189 (1955).

41. Thewlis, J., Acta Cryst., 5, 790 (1952).

42. Alberman, K. B. and J. S. Anderson, J. Chem. Soc., Suppl. Issue No. 1, S 303 (1949).

43. Lehr, P. and J. Langeron, Comp. rend., 241, 1130 (1955).

44. Bowles, J. S. and J. K. MacKenzie, Acta Met., 2, 129 (1954).

45. MacKenzie, J. K. and J. S. Bowles, Acta Met., 2, 138 (1954).

46. Bowles, J. S. and J. K. MacKenzie, Acta Met., 2, 224 (1954).

47. MacKenzie, J. K. and J. S. Bowles, Acta Met., 5, 137 (1957).

48. Christian, J. W., J. Inst. Metals, 84, 386 (1956).

ACKNOWLEDGEMENTS

The author is greatly indebted to Dr. Premo Chiotti not only for technical assistance and direction in the course of this work, but also for inspiration and guidance as teacher, research Group Leader, and Major Professor over a period of four years.

The assistance given in various phases of apparatus construction, experimentation, and particularly in carrying out of the x-ray calculations by Mr. Robert White, Mr. Floyd Gillen, Miss Florence Metz, Mr. Earle Ryba and Mr. Gene Downs is gratefully acknowledged. In addition, the value of numerous discussions of the problems at hand with members of the senior staff and fellow graduate students can not be neglected.

35. Glen, J. W. and S. F. Pugh, "Transformations Between Hexagonal and Body Centered Cubic Lattices", Atomic Energy Research Establishment, Harwell, Berkshire, England, Report No. A.E.R.E. M/R 1144, 1953.

36. Fisher, J. C. and D. Turnbull, Acta Met., 1, 310 (1953).

37. Patel, J. R. and M. Cohen, Acta Met., 1, 531 (1953).

38. Moore, G. E. and K. K. Kelley, J. Amer. Chem. Soc., 69, 2105 (1947).

39. Austin, J. B. and R. L. Rickett, Metals Technology, 5, Tech. Publ. No. 964 (1938).

40. Chubb, W., J. Metals, 7, 189 (1955).

41. Thewlis, J., Acta Cryst., 5, 790 (1952).

42. Alberman, K. B. and J. S. Anderson, J. Chem. Soc., Suppl. Issue No. 1, S 303 (1949).

43. Lehr, P. and J. Langeron, Comp. rend., 241, 1130 (1955).

44. Bowles, J. S. and J. K. MacKenzie, Acta Met., 2, 129 (1954).

45. MacKenzie, J. K. and J. S. Bowles, Acta Met., 2, 138 (1954).

46. Bowles, J. S. and J. K. MacKenzie, Acta Met., 2, 224 (1954).

47. MacKenzie, J. K. and J. S. Bowles, Acta Met., 5, 137 (1957).

48. Christian, J. W., J. Inst. Metals, 84, 386 (1956).

ACKNOWLEDGEMENTS

The author is greatly indebted to Dr. Premo Chiotti not only for technical assistance and direction in the course of this work, but also for inspiration and guidance as teacher, research Group Leader, and Major Professor over a period of four years.

The assistance given in various phases of apparatus construction, experimentation, and particularly in carrying out of the x-ray calculations by Mr. Robert White, Mr. Floyd Gillen, Miss Florence Metz, Mr. Earle Ryba and Mr. Gene Downs is gratefully acknowledged. In addition, the value of numerous discussions of the problems at hand with members of the senior staff and fellow graduate students can not be neglected.